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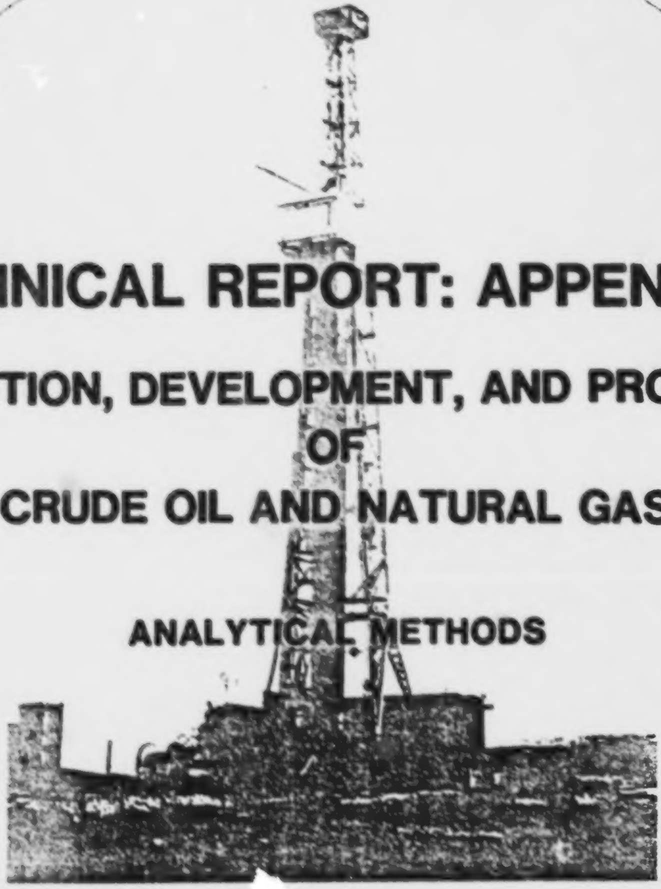

TECHNICAL REPORT: APPENDIX D

EXPLORATION, DEVELOPMENT, AND PRODUCTION OF CRUDE OIL AND NATURAL GAS

ANALYTICAL METHODS

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16. Abstract (Limit: 200 words)

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ANALYTICAL METHODS
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ANALYSIS CAT.	FRACTION	TECHNIQUE	METHOD	MODIFICATION	PAGE
Organics	Pest./Herb.	GC	1618		D-1
	Volatiles	GCMS	1624C		D-89
	A/B Neutral	GCMS	1625C		D-137
	Dioxins/Furans	GCMS	613M	Cl_4 to Cl_8-10L	D-211
		GCMS	8280M	High Res. MS	D-231
	TCLP	Preparation			D-291
Metals	Mercury	CVAA	245.5		D-301
	Furnace	Digestion	3020		D-307
		FURNAA-Sb	204.2		D-311
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		ICP	200.7M	42 Elem. Scr.	D-335
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8.0 GC ANALYSIS-PHENOXYACID..
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1.0 SUMMARY

1.1 This method is a consolidation of methods 608, 614, 615, 617, 622 and 701 that can be used for the analysis of water, solid and multimedia samples for the parameters listed in Tables 1 through 3. The method has been validated for the analysis of the apolar pesticides, phenoxyacid herbicides, and industrial chemicals listed as analyzable by "GC/EC" and "GC/NPD" in the ITD/RCRA list of analytes (Appendix I).

1.2 Two separate extraction and sample preparation schemes are required in this method. One for apolar organochlorine (Table 1) and organophosphorous analytes (Table 2). The other for phenoxyacid herbicides and their esters (Table 3). The scheme for the preparation and analyses of all of the method parameters is presented in Figure 1.

1.3 The sample is initially split into separate aliquots for work up by the different procedures. Apolar analytes are extracted from liquid samples with methylene chloride using a continuous liquid extractor or are extracted from solid samples with methylene chloride/acetone using a sonicator. The apolar extracts are cleaned using gel permeation chromatography (GPC) followed by adsorbtion chromatography prior to GC analysis. Phenoxyacid herbicides and their esters are extracted from acidified liquid samples with methylene chloride using a continuous liquid extractor or are extracted from acidified solid samples with methylene chloride/acetone using a sonicator. The extracted phenoxyacids are partitioned into aqueous base and their esters are hydrolyzed to the free acids. The acid fractions are combined and derivatized with diazomethane then prepared for analysis using adsorbtion chromatography prior to GC analysis.

1.4 GC analysis is accomplished on "megabore" capillary columns. Apolar analytes are analyzed using both electron capture detection (ECD) (for organochlorine analytes), and flame photometric detection (FPD) (for organophosphates). Derivatized phenoxyacid herbicides are analyzed by using ECD. The primary column for all analytes is the DB-5 (or equivalent), the confirmation column is the SPB-608.

2.0 REAGENTS AND EQUIPMENT

2.1 REAGENTS

2.1.1 Sodium Sulfate - anhydrous reagent grade, heated at 400°C for four hours, or 120°C for 16 hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous granular, catalog No. 3375 or equivalent.

2.1.2 Methylene chloride, hexane, ethyl ether, acetone, isooctane (optional), and methanol: pesticide quality or equivalent. It is strongly suggested that each lot of solvent used be analyzed to demonstrate that it is free of interferences before use.

2.1.3 Primary pesticide and PCB standards will be obtained from the EPA Quality Assurance Materials Bank, Pesticides and Industrial Chemicals Repository, R.T.P., NC for the purpose of traceability. Commercial standard should be used for working solutions but must be shown to be traceable (quantitatively and qualitatively) to EPA standards.

2.1.4 Mercury (optional)

2.1.5 Copper powder (optional), bright and nonoxidized

2.1.6 Concentrated Sodium hydroxide solution (6 N). Dissolve 24g NaOH in reagent water and dilute to 100 mL.

2.1.7 Sulfuric acid solution (1:1 v/v). Slowly add 50 mL H_2SO_4 (Sp. gr. 1.84) to 50 mL of reagent water.

2.1.8 Potassium hydroxide solution (37% w/v). Dissolve 37g of potassium hydroxide in 100 mL of distilled water.

2.1.9 Diol bonded silica 500-mg or 1-g cartridges with stainless steel frits (Analytichem, Harbor City, CA) or equivalent.

2.1.10 Florisil 500 mg cartridges (J.T. Baker), or equivalent.

2.1.11 2,4,5-trichlorophenol for Diol cartridge performance check, Prepare a 0.1 μg/mL solution in acetone.

2.1.12 Reagent water - Reagent water is defined as a water in which no interferent is observed at the method detection limit of any parameter when 1 liter of the reagent water is extracted and prepared using the sample workup procedures for environmental waters.

2.1.13 N-methyl (N-nitroso-p-toluenesulfanamide) (Diazald) fresh and high purity, Aldrich Chemical Co.

2.1.14 Silicic Acid: 100 mesh powder (optional).

2.1.15 Ten percent acetone in hexane (v/v), prepare by adding 10 mL of acetone to 90 mL of hexane.

2.1.16 GPC calibration solutions:

2.1.16.1 Bis(2-ethylhexyl)phthalate/pentachlorophenol solution 4 mg/mL each in methylene chloride.

2.1.16.2 Corn oil - 200 mg/mL in methylene chloride.

2.1.17 Acidified sodium sulfate. Add 0.5 mL H_2SO_4 to 100 grams of sodium sulfate and 30-mL ethyl ether. Completely evaporate the ether and store at 110°C. (Caution: Transfer the acidified sodium sulfate into a different vessel before placing it in the oven. This is required to ensure no flammable ether residue is placed into a hot oven.)

2.1.18 Dilute sodium hydroxide solution (0.1M). Dissolve 4g NaOH in reagent water and dilute to 1.0L.

2.2 APPARATUS AND MATERIALS

2.2.1 Apparatus for determining percent moisture.

2.2.1.1 Oven, drying.

2.2.1.2 Desiccator.

2.2.1.3 Crucibles, porcelain (optional).

2.2.1.4 Aluminum weighing pans (optional).

2.2.2 Sonic cell disruptor, Heat Systems - Ultrasonics, Inc. Model 375C (or equivalent) (375 watt with pulsing capability 1/2" or 3/4" disruptor horn).

2.2.3 Sonabox (or equivalent) for use with disrupter.

2.2.4 Beakers, 400-mL.

2.2.5 Kuderna-Danish (K-D) apparatus.

2.2.5.1 Concentrator tube - 10-mL, graduated (Kontes K-570040-1029, or equivalent).

2.2.5.2 Evaporative flask - 500-mL (Kontes K-470001-0500, or equivalent).

2.2.5.3 Snyder column - three-ball macro (Kontes K-503000-0121, or equivalent).

2.2.6 Powder funnels, 10-cm diameter, for filtration/drying.

2.2.7 Boiling chips

2.2.7.1 Silicon carbide boiling chips (optional) - approximately 10/40 mesh. Heat to 400°C for 30 minutes or solvent rinse before use.

2.2.7.2 Teflon boiling chips (optional). Solvent rinse before use.

2.2.8 Water bath - heated, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

2.2.9 Top loading balance, capable of accurately weighing to ±0.01 g.

2.2.10 Balance-Analytical, capable of accurately weighing to ±0.0001 g.

2.2.11 Nitrogen evaporation device equipped with a heated bath that can be maintained at 35-40°C, N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent).

2.2.12 Vials and caps, 2-mL for GC auto sampler.

2.2.13 Gel permeation chromatography cleanup device: automated system. Gel permeation chromatograph (GPC) Analytical Biochemical Labs, Inc., GPC Autoprep 1002 (or equivalent) including:

2.2.13.1 25-mm ID x 600 - 700-mm glass column packed with 70 g of Bio-Beads SX-3, Bio-Rad Laboratories (or equivalent).

2.2.13.2 Syringe, 10-mL with luer lock fitting.

2.2.13.3 Syringe filter holder, stainless steel, and filters - TFE (Gelman 4310 or equivalent) or glass fiber.

2.2.13.4 UV detection (optional) Type 6, 254-mμ Isco, Inc., Lincoln, NB (or equivalent).

2.2.14 Vacuum system for eluting multiple cleanup cartridges.

2.2.14.1 Vac Elute Manifold (Analytichem International, Harbor City, CA, J.T. Baker or Supelco) or equivalent.

2.2.14.2 Vacuum trap made from a 500-mL sidearm flask fitted with a 1 hole stopper and glass tubing.

2.2.14.3 Vacuum pressure gauge.

2.2.14.4 Rack for holding 10-mL volumetric flasks in the manifold.

2.2.15 Pyrex glass wool.

2.2.16 Bottle or test tube, 50-mL with Teflon lined screw cap for sulfur removal.

2.2.17 Separatory funnels - 1000-mL, 500-mL and 250-mL with Teflon stopcocks.

2.2.18 Drying column - Chromatographic column approximately 400-mm long x 19-mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)

2.2.19 Continuous liquid-liquid extractors for use with methylene chloride with Teflon or glass connecting lines. Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NH P/N 6841-10 (or equivalent).

2.2.20 Glass scintillation vials, at least 20-mL, with screw cap and Teflon or aluminum foil liner.

2.2.21 Spatula. Stainless steel or Teflon.

2.2.22 pH Paper. Wide range, Hydrion Papers, Microessential Laboratory, Brooklyn, N.Y. (or equivalent).

2.2.23 Pipet, Volumetric 1.00-mL (optional).

2.2.24 Syringe, 1.00-mL (optional).

2.2.25 Flask, Volumetric 10.00-mL.

2.2.26 Vials, 10-mL, with screw cap and teflon liner (optional).

2.2.27 Tube, centrifuge, 12 to 15-mL with 19-mm ground glass joint, (optional).

2.2.28 Snyder Column, micro with a 19-mm ground glass joint.

2.2.29 Centrifuge, table top (optional).

2.2.30 Centrifuge bottle: 500-mL (Pyrex 1260 or equivalent).

2.2.31 Diazald kit with clear seal joints for generation of diazomethane, Aldrich Chemical Co., catalog No. Z10, 025-0.

2.2.32 Flask, filter, 1-L.

2.2.33 Funnel, Buchner, 15-cm.

2.2.34 Paper, filter (Whatman #1, or equivalent), 15-cm.

2.2.35 Gas chromatographic system including two 0.25-inch injectors, detection makeup gas, an electron capture detector, and a flame photometric detector. It is recommended that the GC be equipped with an integrator or data system rather than a strip chart recorder.

2.3.36 pH Meter with a combination glass electrode.

2.3.37 Megabore capillary column chose two.

2.3.37.1 DB-5 (J&W Scientific) or a SP-5 (Supelco Inc.) or equivalent.

2.3.37.2 DB-608 (J&W Scientific) or equivalent.

2.3.37.3 SPB-608 (Supelco Inc.) or equivalent.

3.0 EXTRACTIONS-APOLAR

3.1 OVERVIEW

3.1.1 Aqueous samples are extracted using methylene chloride in a continuous liquid-liquid extractor. Extracts are then dried and concentrated by Kuderna-Danish techniques in preparation for cleanup (Section 4) and analysis (Section 5).

3.1.2 Soil or sediment samples are mixed with sodium sulfate and extracted using a 1:1 acetone:methylene chloride solvent by a sonication technique. Extracts are then filtered, dried, concentrated by Kuderna-Danish, and solvent exchanged to methylene chloride in preparation for GPC cleanup (4.2).

3.1.3 Most sludge samples are treated as solid samples (3.3) and 30 g samples are extracted using sonication with methylene chloride/acetone. Some sludge samples may be treated as liquids (3.2). In that case, 30 g samples are added to a 1 L of reagent water and extracted with a continuous extractor.

3.2 APOLAR PROTOCOL FOR LIQUIDS

3.2.1 Summary of Sample Preparation Method

3.2.1.1 A 1 L volume of a water sample or a mixture of 30 g of sludge and 1 L of reagent water is extracted with methylene chloride using a continuous extractor. The methylene chloride extract is dried, concentrated, exchanged to hexane, and adjusted to a volume of 10.0 mL and a 1.0 mL aliquot is cleaned up on a Diol cartridge prior to GC analysis. Optional GPC (4.2) and sulfur cleanup (4.4) techniques are also allowed.

3.2.2 Liquid Sample Extraction.

3.2.2.1 Liquid samples must be extracted using continuous extraction.

3.2.2.2 With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and water layers in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction. Any sample in which solids precipitate through the glass wool must be treated as solids (3.3).

3.2.2.3 The percent weight loss of volatiles from sludge must be determined and reported according to the procedures described in 3.3.1.3.

3.2.2.4 After the sample has been transferred to the extractor, measure and record the pH with wide range pH paper and adjust to between pH 5 and 9 with 6 N sodium hydroxide or 1:1 sulfuric acid solution, if required. Record and report which samples require pH adjustment.

3.2.2.5 Add sufficient methylene chloride to the distilling flask to ensure proper solvent cycling during operation and extract for 18 hours.

3.2.3 Extract Drying and Concentration

3.2.3.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Pour the combined extract through anhydrous sodium sulfate and collect the extract in the K-D concentrator (the sodium sulfate can be held in a drying column filled to a height of about 20-cm or in a powder funnel plugged with glass wool filled to a height of 4-5-cm [3.3.2.5]). Rinse the Erlenmeyer flask and column with at least one additional 20 to 30 mL portion of methylene chloride to complete the quantitative transfer.

3.2.3.2 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. Do not allow the evaporator to go dry.

3.2.3.3 If GPC cleanup is to be used, remove the Snyder column, rinse the flask and its lower joint into the concentrator tube, adjust the volume to 10.0 mL with methylene chloride and proceed to Section 4. If no GPC cleanup is required, proceed with the hexane exchange described below.

3.2.4 Exchange into Hexane

3.2.4.1 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes. Do not allow the evaporator to go dry.

3.2.4.2 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane and proceed to Section 4 for Diol cartridge cleanup.

3.3 APOLAR PROTOCOL FOR SOLIDS

3.3.1 Sample Preparation

3.3.1.1 Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase. The lab must estimate to the nearest 10 percent (by weight) the amount of water decanted (and discarded) from the sample and report that value with the data.

3.3.1.2 Transfer 30 g of a soil, sediment or sludge sample to 100-mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample using a glass electrode and pH meter while the sample is stirring. Report pH value with the data, but do not attempt to adjust the pH of the sample before extraction. Discard the portion of the sample used for pH determination.

3.3.1.3 Transfer 5 to 10 g of the sediment into a tarred crucible or aluminum weighing pan and weigh to the nearest 0.01 g. Transfer the sediment and weighing pan into an oven monitored at 105°C and dry overnight. Allow the sample and weighing pan to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the nonvolatiles in the sample. (Caution: Gases volatilized from some soil/sediment samples may require that this drying procedure be carried out in a hood.)

$$\frac{\text{wt of sample - wt of heated sample}}{\text{wt of sample}} \times 100 = \%\ \text{weight loss} \quad (3.1)$$

3.3.2 Extraction with Sonic Agitation

3.3.2.1 Weigh approximately 30 g of sample (to the nearest 0.1 g) into a 400-mL beaker and add 60 g of anhydrous sodium sulfate and mix thoroughly to give a homogeneous mixture.

3.3.2.2 Some wet sludge samples may require more than 60 g of sodium sulfate. The laboratory is required to add sufficient sodium sulfate to adsorb all of the water in the sample prior to adding organic solvent.

3.3.2.3 Immediately add 80 mL of 1:1 methylene chloride:acetone mixture to the sample.

3.3.2.4 Place the sonicator probe about 1/2 inch below the surface of the solvent but above the sediment layer.

3.3.2.5 Sonicate for 3 min., using the 3/4 inch horn at full power with pulse set at 50 percent. Do not use a microtip.

3.3.2.6 Prepare a filtration/drying bed by placing a plug of glass wool in the neck of a 10-cm powder funnel and filling the funnel to approximately half its depth (4 or 5 cm) with anhydrous sodium sulfate. Decant the extract through the packed funnel and collect it in a 500-mL evaporation (K-D) flask.

3.3.2.7 Repeat the extraction two more times with fresh 80 mL portions of the 1:1 methylene chloride:acetone mixture. Decant the extraction solvent after each sonication. After the final sonication, pour the entire sample into the funnel and rinse with 60-mL portion of 1:1 methylene chloride:acetone mixture.

3.3.2.8 Some samples may require additional clarification before evaporation. These should be vacuum filtered through Whatman #1 paper using a Buchner funnel then transferred to a K-D apparatus.

3.3.2.9 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. In order to remove as much acetone as possible, reduce the apparent volume of liquid to less than 3 mL, but do not take to dryness. Remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Make up a 10 mL final volume with methylene chloride.

Proceed to Part 4.1 for mandatory GPC cleanup.

4.0 EXTRACT CLEANUP-APOLAR

4.1 REQUIREMENTS

4.1.1 GPC cleanup is mandatory for all apolar analyses of soil/sediment and sludge extracts. It can also be used for water samples, if needed. GPC removes many higher molecular weight contaminants which would otherwise accelerate degradation of gas chromatography columns and thus reduce instrument performance. The GPC must meet monthly performance checks.

4.1.2 Diol cartridge cleanup is required for all extracts. It removes polar organic molecules such as phenols. Each lot number of Diol cartridges must pass a cartridge performance check.

4.1.3 Sulfur can be removed by one of two methods, according to laboratory preference. Chromatogram interference due to sulfur is not acceptable.

4.2 EXTRACT CLEANUP BY GEL PERMEATION CHROMATOGRAPHY (GPC)

4.2.1 GPC Setup, Operation and Initial Calibration

4.2.1.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400-mL beaker. Allow the beads to swell overnight in methylene chloride before packing the column. Transfer the swelled beads to the column and begin pumping solvent through the column, from bottom to top, at a rate of 5.0 mL/min. After approximately 1 hour, adjust the pressure on the column to between 5 and 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 5 to 10 psi.

4.2.1.2 NOTE: The description of solvent flow rate and column pressure applies only to the ABC GPC apparatus. Laboratories using equivalent equipment must develop the parameters for their apparatus which give acceptable performance (described in Section 4.2.2).

4.2.1.3 The SX-3 Bio Beads column may be used for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flow rate remains constant. The calibration must be checked periodically, not less than once every 30 days, using standard pesticide and PCB mixtures.

4.2.1.4 NOTE: Some samples should be centrifuged and/or filtered through an inert filter held in a 25-mm stainless steel holder before loading onto the GPC in order to remove particulate matter.

4.2.1.5 Load the 5.0-mL sample loop using 7.5 mL of the concentrate of the extract of each soil sample (described in 3.3.2.) and of those water samples (described in 3.2.2 or 3.2.3.) to be cleaned up by GPC.

4.2.1.6 NOTE: Some samples may have to be loaded into two or more loops in order to prevent overloading the GPC column. All highly viscous samples or samples known to contain $>$ 1 g of nonvolatile residue should be diluted to 15 mL using methylene chloride and loaded into two loops or to 22.5 mL and loaded into three loops.

4.2.1.7 Set the instrument terminal for the appropriate number of samples; set the length of the dump, collect and wash cycles for the number of minutes determined by either of the calibration procedures described below in 4.2.1.9 or 4.2.1.10. Set up and label one collection flask for each loop by placing the appropriate Teflon effluent line into the flask, then covering the flask with aluminum foil. Begin pumping methylene chloride through the column at 5 mL/min. (5 to 10 psi), allow the flow to stabilize for at least 15 minutes, then begin the automatic cleanup sequence by pressing the "auto start" button.

4.2.1.8 After the appropriate GPC fraction has been collected for each sample, evaporate the methylene chloride and exchange to hexane as described in 3.2.5.

4.2.1.9 Two alternate GPC calibration procedures are described below, one of these two must be used. The first is based on a combination of gravimetric and GC analysis of collected GPC fractions, the second is based on monitoring the elution of standards with a UV detector connected to the GPC column. If the UV technique is chosen, care must be taken to account for any difference in volume (elution time) between the GC column and the detector and the GPC column and the collection vial.

4.2.2 Gravimetric GPC Calibration Procedure

4.2.2.1 Set the "dump", "collect" and "wash" times for 00, 02, and 00 minutes, respectively. Set the terminal for 20 samples.

4.2.2.2 Under each of the first twenty receiver lines, place a tared 20-mL scintillation vial.

4.2.2.3 Into Sample No. 1 load 5 mL of 200-mg/mL corn oil solution.

4.2.2.4 Start the auto sequence, collect twenty 10-mL fractions (40 min.).

4.2.2.5 Passively evaporate each fraction to dryness in a fume hood (overnight).

4.2.2.6 Reweigh the vials and record the net weight gain.

4.2.2.7 Plot weight of the elute vs. time to determine the elution profile.

4.2.2.8 Reset the sampling position to 00.

4.2.2.9 Into Sample Loop No. 1, load 5 mL of 0.4-mg/mL PCP/Phthalate Solution.

4.2.2.10 Set the "collect" time to 03 minutes.

4.2.2.11 Under each of the first twenty receiver lines place a clean 20-mL scintillation vial. (NOTE: The vials need not be tared.)

4.2.2.12 Start the auto sequence, collect twenty 15-mL fractions (1 hour).

4.2.2.13 Analyze each fraction by GC to determine the amount of PCP and phthalate.

4.2.2.14 Plot the amounts of PCP and phthalate to determine the elution profiles.

4.2.2.15 Choose the "DUMP" time such that 85+ percent of phthalate is recovered and the corn oil is discarded.

4.2.2.16 Choose the "COLLECT" time to extend 10 minutes after the elution of PCP and set a "WASH" time of 10 minutes.

4.2.3 UV Detector Calibration Procedure

4.2.3.1 Connect the end of the column to a UV detector (254 nm).

4.2.3.2 Zero the detector and start the strip chart recorder.

4.2.3.3 Into Sample Loop No. 1 load 5 mL of 20-mg/mL corn oil solution and into Sample Loop No. 2 load 5 mL of 0.4-mg/mL PCP/phthalate. (NOTE: The corn oil concentration used in this UV procedure is a 10-fold dilution of that used in the gravimetric method.)

4.2.3.4 Inject Sample Loop No. 1, note the injection on the strip chart recorder.

4.2.3.5 After the corn oil elutes, allow the recorder to continue for a few minutes to again establish a baseline.

4.2.3.6 Inject Sample Loop No. 2 and note the injection on the strip chart recorder.

4.2.3.7 Determine the elution times for the corn oil, PCP and phthalate.

4.2.3.8 Choose a "DUMP" time which removes the corn oil yet recovers >85 percent of the phthalate. Choose a "COLLECT" time which continues 10 minutes beyond the elution of pentachlorophenol and a "WASH" time of 10 minutes.

4.2.3.9 NOTE: The DUMP and collect times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

4.2.4 Continuing GPC calibration requirement.

4.2.4.1 At least once ever 30 days, the calibration of the GPC must be verified by determining the recovery of 10 method analytes (Tables 1 and 2).

4.2.4.2 The ten analytes used are chosen by each lab. The choice is based on which analytes that were most often detected in their samples during the previous month.

4.2.4.3 The GPC calibration solution is prepared so that the concentration of each analyte is between 0.5 and 5 µg/mL.

4.2.4.4 Using 7.5 mL of the calibration solution loaded into a GPC loop and a fraction using the GPC program established using either of the described procedures (4.2.2 or 4.2.3).

4.2.4.5 The collected GPC calibration fraction is transferred quantitatively to a K-D apparatus and the volume of methylene chloride is reduced (3.2.3). After cooling, the solvent is exchanged to hexane (3.2.4). The final volume is adjusted to 10.0 mL and the sample is analyzed by GC according to the procedures in Section 5.

4.2.4.6 The GPC performance is acceptable if all of the analytes are recovered at 85-110 percent and the column can continue to be used. If the recovery is less than 85 percent, or more than 110 percent, the column must be repacked (4.2.1) and recalibrated before more samples are run.

4.3 DIOL CARTRIDGE CLEANUP

4.3.1 Cartridge Performance Check

Every lot number of Diol cartridges must be tested. A lot of Diol cartridges is demonstrated as acceptable if all apolar analytes are recovered at 80-110 percent and if trichlorophenol is not detected when the compounds are eluted through a cartridge using the method described in 4.3.4.

4.3.2 Nitrogen Blowdown Technique (Taken from ASTM Method D 3086)

4.3.2.1 Place the concentrator tube in a heating bath (35°C) and evaporate the solvent to the final volume using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). The extract must never be allowed to become dry.

4.3.2.2 CAUTION: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane then dried prior to use.

4.3.3 Extract Preparation

4.3.3.1 For samples which have been run through the GPC cleanup solvent, exchange to hexane (3.2.4) and adjust the hexane extract volume to 5.0 mL using nitrogen blowdown described in 4.3.2. For those aqueous samples not passed through the GPC step, adjust to 10.0 mL. The different final volumes are required because only half of the methylene chloride concentrates are recovered from the GPC cleanup.

4.3.4 Diol Cartridge Cleanup

4.3.4.1 Attach the Vac-Elute vacuum manifold to a water aspirator or a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5 and 10 pounds of vacuum.

4.3.4.2 Most liquid samples can be cleaned using a 500-mg Diol cartridge, the cleanup of soil and sludge extracts must be accomplished using 1 g cartridges.

4.3.4.3 Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (9:1). This is accomplished by placing the cartridge in the vacuum manifold, pulling a vacuum and passing 5 mL of the hexane/acetone solution through the cartridge.

4.3.4.4 After the cartridges in the manifold are washed, the vacuum is released and a rack containing labeled 10-mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.

4.3.4.5 After the volumetric flasks are in place, vacuum to the manifold is restored and a volume of 1.0 mL from each sample, blank or matrix spike extract to be analyzed is transferred to the top frit of the appropriate Diol cartridge.

4.3.4.6 NOTE: Because the volumes marked on concentrator tubes are not necessarily accurate, the use of an 1.00-mL syringe or a volumetric pipet is required.

4.3.4.7 The analytes in the extract concentrates are then eluted through the column with 9 mL of hexane/acetone (9:1) and collected into the 10-mL volumetric flasks held in the rack inside the vacuum manifold.

4.3.4.8 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10-mL vial. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the cartridge eluate.

4.3.4.9 Concentrate the extract to 1.0 mL using nitrogen blow-down (described in 4.3.2).

4.3.4.10 If crystals of sulfur are evident or sulfur is suspected to be present, proceed to Section 4.4.

4.3.4.11 If the sulfur is not expected to be a problem, transfer the 1.0-mL concentrate to a GC vial and label the vial. The extract is ready for GC analysis, proceed to Section 5. Store the extracts at 4°C in the dark until analyses are performed.

4.4 SULFUR REMOVAL

4.4.1 Two options are available for the removal of sulfur from samples. The mercury technique appears to be the most reliable, but requires the use of small volumes of mercury in the laboratory.

4.4.2 CAUTION: Mercury containing waste should be segregated and disposed of properly.

4.4.3 Mercury Technique

4.4.3.1 Add 1 to 3 drops of mercury for each 1-mL hexane extract in a clean vial. Seal the vial and agitate for 30 seconds. Filter or centrifuge and decant to remove all solid precipitate and liquid mercury. Analyze the extract if the mercury appears shiny. If the mercury turns black, repeat as necessary. Dispose of the mercury waste properly.

4.4.3.2 If only a partial set of samples requires sulfur cleanup, an additional reagent blank is not required.

4.4.4 Copper Technique

4.4.4.1 Bright (non-oxidized) granular copper can be used in place of mercury in the procedure described in Section 4.4.3.1.

5.0 GC ANALYSIS-APOLAR

5.1 SUMMARY

5.1.1 Sample extracts are analyzed by both GC/ECD for organochlorine parameters and by GC/FPD for organophosphorous parameters.

5.1.2 The primary column for both organochlorine and organophosphate analysis is a 15 m x 53 mm id DB-5 megabore capillary column (or equivalent).

5.1.3 The secondary column for both organochlorine and organophosphorous analyses is a 15 m x 0.53 mm id SPB-608 or DB-608 megabore capillary column (or equivalent).

5.2 GC CONDITIONS

5.2.1 Megabore capillary columns can be installed in standard 0.25-inch packed column injector and detector ports using suitable glass adapters and graphite ferrules. Because the column flow used is 5 mL/minute, it is necessary to supply a suitable makeup gas to the detector.

5.2.2 Electron capture detectors should be plumbed with helium or hydrogen carrier and P-10 (Argon/methane) as a detector makeup gas, the detector temperature should be 275°C.

5.2.3 Flame photometric detectors should be plumbed with helium or hydrogen carrier and nitrogen as a detector makeup, the detector temperature should be 250°C.

5.2.4 The temperature program for organochlorine analysis is:

T_i = 50°C
Initial time one minute
Initial temperature ramp 20°/min to 150°C
Second temperature ramp 8°/min to 180°C
Third temperature ramp 3°/min to 250°C
Final hold 15 minutes

Note: It may be necessary to adjust this temperature program for individual gas chromatographs.

5.2.5 The temperature program for organophosphorous analysis is:

T_i = 50°C
Initial time one minute
Initial temperature ramp 5°/min to 140°C, hold 10 minutes
Second temperature ramp 10°/min to 250°C
Five minute final hold.

Note: It may be necessary to adjust this temperature program for individual gas chromatographs.

5.2.6 Injectors should be set at 260°C.

5.3 CALIBRATION

5.3.1 After establishing the appropriate GC operating conditions (5.2) for the method parameters, calibrate the GC system using the external standard technique.

5.3.2 For each parameter of interest, prepare working standards at three concentration levels over a range of a least two orders of magnitude. The low concentration should be near to, but above, the method detection limit (Section 5.7). The medium concentration must be at least 10 times the low concentration and the high concentration must be at least 10 times the medium concentration (at least 100 times the low concentration). These concentrations define the calibration range in which analytes can be quantitated.

5.3.3 Three-point instrument calibration based on peak height or peak area is required for each single component pesticide. The laboratory has 3 choices on how to establish three point calibration. Only one of the three calibration methods can be used to quantitate samples in any single run sequence. laboratories cannot mix calibration techniques for samples quantitated using a single initial calibration.

5.3.4 The laboratory can use a mean calibration factor ($\overline{CF}$) determined from the three concentration but only if the % RSD for the three points is <10 percent.

$$\overline{CF} = 1/3 \sum_{i=1}^{N} \frac{\text{Peak area (or height of the standard)}}{\text{Mass injected (ng)}} \qquad (5.3)$$

$$\%RSD = \frac{SD}{\overline{CF}} \times 100 \qquad (5.4)$$

$$\text{where } SD = \sqrt{\frac{\sum_{i=1}^{N} (CF_i - \overline{CF})^2}{N-1}} \qquad (5.5)$$

N=3

5.3.5 The laboratory can use a calibration line drawn through all three calibration points only if their value (coefficient of determination) from the linear regression calculation is >0.975.

5.3.6 Laboratories with electronic integrators or data systems that automatically calculate calibration curves as line segments between calibration points and the origin may use line segment calibration curves for each single component analyte. This technique may be used only if the r value (coefficient of determination) from the linear regression calculation is >0.975 for all three points for each single component analyte.

5.3.7 Sample analysis may not proceed until a satisfactory calibration has been demonstrated.

5.3.8 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, a new calibration curve or calibration factor must be prepared for that parameter.

5.4 QUANTITATION OF ANALYSES

5.4.1 Analytes can be quantitated using either manual measurement of onscale chromatograms, with a modern electronic integrator, or with a laboratory data system. The analyst can use either peak height or peak area as the basis for quantitation. The use of electronic integration or a laboratory data system is strongly recommended.

5.4.2 If manual quantitation is used, all peaks used for calibration and for sample analysis must be onscale and give at least 20 percent deflection from baseline at maximum height. Guidance in the manual quantitation of peaks is given in the EPA MANUAL OF ANALYTICAL METHODS FOR THE ANALYSIS OF PESTICIDES IN HUMANS AND ENVIRONMENTAL SAMPLES, EPA-600/8-80-038, or in the FDA Pesticide Analytical Manual.

5.4.3 If electronic integration is used, it is the responsibility of the analyst to be sure that the integration parameters are set properly and that off-scale chromatograms are within the dynamic range of the device. The analyst should also check for data flags that indicate improper quantitation of peaks prior to reporting data to the EPA. In addition, the peak width of identified analytes must not be more than 2.0 times the width of the high concentration calibration peak(s) for the same analyte.

5.4.4 The detector response (peak area or peak height) to all of the analytes must lie between the response of the low and high concentrations in the three-point initial calibration in order to be quantitated.

5.4.5 The concentration of the single component analytes are calculated using the following equations:

5.4.5.1 Water

$$\text{concentration} \quad \mu g/L = \frac{(A_x)(V_t)}{(CF)(V_i)(V_x)} \qquad (5.10)$$

Where:

A_x = Response for the parameter to be measured.

CF = Calibration factor for the external standard (5.3.3).

V_t = Volume of total extract (μL) (take into account any dilution).

V_i = Volume of extract injected (μL).

V_x = Volume of water extracted (mL).

5.4.5.2 Sediment/Soil

$$\text{Concentration} \quad \mu g/kg = \frac{(A_x)\ (V_t)}{(CF)\,(V_i)\,(W_s)\,(D)} \qquad (5.10)$$

(Dry weight basis)

Where:

A_x, CF, V_i = same as given above in 5.3.4.1

$D = \dfrac{100 - \text{percent weight loss}}{100}$ (percent weight loss from Section 3.3)

W_s = Weight of sample extracted (g).

5.4.6 The quantitation of multicomponent pesticide/PCBs must be accomplished by comparing the sum of the heights or the areas of at least three major peaks of the multicomponent analyte in the sample compared with the same peaks in the standard. The concentration of multicomponent analytes are also calculated using equations 5.10 and 5.11 where A_x is the sum of the major peaks of the multicomponent analyte.

5.4.7 The identification and quantitation of multicomponent analytes may be complicated by the environmental alteration of the peak pattern of multicomponent pesticides/PCBs, and by the presence of coeluting analytes and/or matrix interference.

5.4.8 If more than one multicomponent is observed in a sample, the laboratory must chose separate peaks to quantitate the different multicomponent analytes. A peak common to both analytes present in the sample must not be used to quantitate both compounds in the same sample.

5.5 Scheme of Analysis.

5.5.1 A flow scheme for the analysis of samples by this procedure are given in Figure 1.

5.6 Sample chromatograms.

5.6.1 Sample chromatograms of mixtures containing all single component analytes and of all multicomponent analytes for both columns are presented in Figures 2-23.

5.7 Method Detection limits.

5.7.1 Any method is dependent on the complexity of the sample matrix analyzed, but this procedure can be used to determine all of the single component apolar organochlorine analytes (Table 1), except diallate to a detection limit of <5 ppb. If greater sensitivity is required, the 9 mL of extract not subjected to Diol cleanup (4.3) can be blown down to 1 mL (4.3.2) and cleaned on a 1 g Diol column. This concentrate can be used to give a method detection limit of <0.5 ppb.

5.7.2 The procedure can be used to determine all of the single component apolar organophosphate analytes (Table 2) to a detection limit of <50 ppm. If greater sensitivity is required, the 9 mL of extract not subjected to Diol cleanup

(4.3) can be blown down to 1 mL and cleaned on a 1 g Diol column. This concentrate can be used to give a method detection limit of <5 ppb.

6.0 EXTRACTION-PHENOXYACIDS

6.1 OVERVIEW

6.1.1 Phenoxyacids and their esters are extracted from acidified aqueous samples using methylene chloride using a continuous liquid extractor.

6.1.2 Acids and esters are extracted from acidified solid samples using methylene chloride/acetone and a sonicator.

6.1.3 Most sludge samples are treated as solid samples (6.3) and 30 g samples are extracted with methylene chloride/acetone with a sonicator. Some sludge samples may be treated as liquid (6.2). In that case, 30 g are added to 1 L of reagent water and extracted using a continuous extractor.

6.1.4 The sample extracts are reduced in volume using a K-D apparatus, the free phenoxyacid herbicides are partitioned into aqueous base and the esters into methylene chloride. The esters are hydrolyzed using aqueous potassium hydroxide and neutral organics are partitioned into methylene chloride and discarded. The two basic aqueous fractions containing phenoxyacids are combined, acidified, and the acids are extracted into methylene chloride. The phenoxyacids are then derivitized with diazomethane and analyzed by GC/ECD.

6.2 LIQUID SAMPLE EXTRACTION-PHENOXYACID

6.2.1 Liquid samples must be extracted using continuous extraction. Using a 1 liter graduated cylinder, measure out a 1 liter sample aliquot and place it into the continuous extractor.

6.2.2 With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and water layers in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction. Any sample in which solids precipitate through the glass wool must be treated as solids (6.3).

6.2.3 The percent weight loss of volatiles from sludge must be determined and reported according to the procedure described in Section 6.3.1.3.

6.2.4 After the sample has been transferred to the extractor, measure and record the pH of the sample with wide range pH paper and adjust to below 2 with 1:1 sulfuric acid, if required (Caution: some samples should be acidified in the hood because of the potential for generating hydrogen sulfide).

6.2.5 Add sufficient methylene chloride to the distilling flask to ensure proper cycling during operation and extract for 18 hours.

6.2.6 If solids are present in the methylene chloride, after extraction, filter the organic phase through Watman #1 paper.

6.2.7 Transfer the methylene chloride fraction to a 500 mL separatory funnel and proceed to the separation of the phenoxyacids and phenoxyesters (6.4).

6.3 SOLID SAMPLE EXTRACTION-PHENOXYACID

6.3.1 Sample Preparation

6.3.1.1 Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase. The lab must estimate to the nearest 10 percent (by weight) the amount of water decanted (and discarded) from the sample and report that value on the data sheet.

6.3.1.2 Transfer 30g of sample to a 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample using a glass electrode and pH meter while the sample is stirring. Report pH value with the data, then determine the amount of 1:1 sulfuric acid/water required to reduce the pH to <2. Discard the portion of the sample used for pH determination.

6.3.1.3 Transfer 5 to 10 g of the sediment into a tarred crucible or aluminum weighing pan and weigh to the nearest 0.01 g. Transfer the sediment and weighing pan into an over monitored at 105°C and dry overnight. Allow the sample and weighing pan to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment. (Caution: Gases volatilized from some soil/sediment samples may require that this drying procedure be carried out in a hood.)

$$\frac{\text{wt of sample - wt of dry sample}}{\text{wt of sample}} \times 100 = \%\text{ weight loss} \quad (6.1)$$

6.3.2 Extraction with Sonic Agitation

6.3.2.1 Weigh approximately 30 g of sample (to the nearest 0.1-g) into a 400-mL beaker.

6.3.2.2 Add the amount of 1:1 sulfuric acid/water determined in 6.3.1.2 (Caution: some samples may evolve toxic gases on the addition of acid).

6.3.2.3 Add 60 g of acidified sodium sulfate.

6.3.2.4 Some wet sludge samples may require more than 60 g of acidified sodium sulfate. The laboratory is required to add sufficient acidified sodium sulfate to adsorb all of the water in the sample prior to adding organic solvent.

6.3.2.5 Immediately add 80 mL of 1:1 methylene chloride:acetone mixture to the sample.

6.3.2.6 Place the sonicator probe about 1/2 inch below the surface of the solvent but above the sediment layer.

6.3.2.7 Sonicate for 3 min., using the 3/4 inch horn at full power with pulse set at 50 percent. Do not use a microtip.

6.3.2.8 Caution - the sonicator horn must be cleaned in 5% aqueous sodium bicarbonate and methanol between samples. If acid is allowed to remain on the horn, it will be damaged.

6.3.2.9 Prepare a filtration/drying bed by placing a plug of glass wool in the neck of a 10-cm powder funnel and filling the funnel to approximately half its depth (4 or 5 cm) with acidified sodium sulfate. Decant the extract through the packed funnel and collect it in a 500-mL evaporation (K-D) flask, or a 500 mL centrifuge bottle.

6.3.2.10 Repeat the extraction two more times with fresh 80 mL portions of the 1:1 methylene chloride:acetone mixture. Decant the extraction solvent after each sonication. After the final sonication, pour the entire sample into the funnel and rinse with a 60-mL portion of the 1:1 methylene chloride:acetone mixture.

6.3.2.11 If required, centrifuge the combined extract for 10 minutes to settle fine particles then filter the extracts through Whatman #1 filter paper into a 500 mL K-D flask.

6.3.2.12 Transfer the methylene chloride fraction to a 500 mL separatory funnel prior to the separation of the phenoxyacids and phenoxyesters.

6.4 ESTER HYDROLYSIS

6.4.1 Extract the organic phase of the phenoxyacid preparation two times with 100 mL portions of 0.1 N aqueous sodium hydroxide. Combine the aqueous (top) layers containing the free acid herbicides in a beaker and save. The organic (bottom) layer contains the herbicide esters, which must be hydrolyzed.

6.4.2 Transfer the methylene chloride layer into 500-mL Kuderna-Danish flask. Add boiling chips to the K-D and fit it with a three-ball Snyder columns. Wet the Snyder column with 1 mL of methylene chloride and reduce the methylene chloride to a volume of approximately 25 mL on the water bath.

6.4.3 Remove the flask from the water bath and allow it to cool. Then add 5 mL of 37% aqueous potassium hydroxide, 30 mL of distilled water and 40 mL of methanol to the flask.

6.4.4 Add additional boiling chips to the flask. Reflux the mixture in the K-D on the water bath for 2 hours. Remove the flask from the water bath and cool to room temperature.

6.4.5 Transfer hydrolysate from the K-D flask to a 250 mL separatory funnel. Extract the aqueous residue with 50 mL of methylene chloride and discard the methylene chloride (bottom layer) which contains neutral interferents.

6.4.6 At this point the two aqueous solutions containing the free herbicide salts from 6.4.1 and 6.4.5 can be combined (they can be analyzed separately, if required).

6.4.7 Add sulfuric acid to the basic aqueous solutions to adjust the pH to ≤ 1.

6.4.8 Transfer the acidified aqueous solution into a 500 mL separatory funnel and extract the solution three times with 100 mL portions of methylene chloride.

6.4.9 Combine the organic extracts in 500 mL Kuderna-Danish flasks. Add boiling chips to the extracts in the flasks and fit them with three-ball Snyder columns.

6.4.10 Evaporate the methylene chloride to approximately 5 mL on a hot water bath (the samples may be stored at this stage).

6.4.11 Remove the flasks from water bath. Evaporate the extracts just to dryness under a stream of nitrogen.

6.4.12 Re-dissolve the extracts in 10 mL of iso-octane.

6.4.13 Transfer 1 mL of the iso-octane solution to a clean vial and add 0.5 mL of methanol and 3 mL of ether. The sample is now ready for methylation with diazomethane (the sample should not be stored overnight at this step).

7.0 ESTERIFICATION

7.1 The diazomethane derivatization procedure described below will produce an efficient reaction with all of the chlorinated herbicides described in this method. It should be used only by an experienced analyst, due to the potential hazards associated with its use.

7.2 Diazomethane is a carcinogen and can explode under certain conditions. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides to reduce potential contact with diazomethane.
- Do not heat above 90°C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper power, calcium chloride, and boiling chips.

7.3 Specific instructions for preparing diazomethane are provided with the generator kit. They must be followed precisely.

7.4 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period. If the yellow color disappears before 10 minutes has passed, add an additional 2 mL of diazomethane solution. Colored or highly complex samples will require at least 4 mL of diazomethane to ensure quantitative reaction of all phenoxyacid herbicides. For these samples, diazomethane must be added until no evolution of nitrogen is observed after the addition of etherial diazomethane.

7.5 After 15 minutes rinse inside wall of ampule with several hundred µL of ethyl ether. Reduce the sample to approximately 1 mL under a stream of nitrogen. Remove any excess diazomethane by reacting it with 10 mg silicic acid.

7.6 Remove all of the solvent under a stream of dry nitrogen (4.3.2). When the vial is just dry, remove it from the nitrogen.

7.7 Immediately transfer the phenoxyesters to an autosampler vial using hexane and adjust the final sample volume to 1.00 mL prior to GC analysis.

8.0 GC ANALYSIS-PHENOXYACIDS

8.1 SUMMARY

8.1.1 Extracts are analyzed by GC/ECD for methyl esters of phenoxyacid herbicides.

8.1.2 The primary column for analysis is a 15 m x 0.53 mm ID DB-5 megabore capillary column (or equivalent).

8.1.3 The secondary column for analyses is a 15 m x 0.53 mm ID SPB-608 or DB-608 megabore capillary column (or equivalent).

8.2 GC CONDITIONS

8.2.1 Megabore capillary columns can be installed in 0.25-inch packed column injector and detector ports using suitable glass adapters and graphite ferrules. Because the column flow used will be approximately 5 mL/minute, it is necessary to supply a suitable makeup gas to the detector.

8.2.2 ECD's should be plumbed with helium or hydrogen carrier gas and P-10 as a detector makeup gas.

8.2.3 The initial temperature program to use for phenoxyacid herbicide analysis on both columns is:

T_i = 50°C
Initial time one minute
Initial temperature ramp 15°/min to 140°C
Second temperature ramp 2°/min to 180°C
Final temperature hold 10 minutes

it may be necessary to adjust the temperature program for individual gas chromatographs.

8.2.4 GC injectors should be set at 260°C.

8.3 CALIBRATION

8.3.1 After establishing the appropriate GC operating conditions (8.2) for the method parameters, calibrate the GC system using the external standard technique.

8.3.2 For each parameter of interest, prepare working standards at three concentration levels over a range of at least two orders of magnitude by reacting solutions of phenoxyacid standards with diazomethane using the procedure described in Section 7.0 (quantitative yield of methyl esters from standards and samples is assumed). The low concentration should be near to, but not above, the method detection limit (8.7). The medium concentration must be at least 10 times the low concentration and the high concentration must be at least 10 times the medium concentration (at least 100 times the low concentration). These concentrations define the calibration range in which analytes can be quantitated.

8.3.3 Three-point instrument calibration based on peak height or peak area is required for each single component pesticide. The laboratory has 3 choices on how to establish three point calibration. Only one of the three calibration methods can be used to quantitate samples in any single run sequence. laboratories cannot mix calibration techniques for samples quantitated using a single initial calibration.

8.3.4 The laboratory can use a mean calibration factor ($\overline{CF}$) determined from the three concentration but only if the % RSD for the three points is <10 percent.

$$\overline{CF} = 1/3 \sum_{i=1}^{N} \frac{\text{Peak area (or height of the standard)}}{\text{Mass injected (ng)}} \tag{5.3}$$

$$\%RSD = \frac{SD}{CF} \times 100 \tag{5.4}$$

$$\text{where } SD = \sqrt{\frac{\sum_{i=1}^{N} (CF_i - \overline{CF})^2}{N-1}} \tag{5.5}$$

$N=3$

8.3.5 The laboratory can use a calibration line drawn through all three calibration points only if their value (coefficient of determination) from the linear regression calculation is >0.975.

8.3.6 Laboratories with electronic integrators or data systems that automatically calculate calibration curves as line segments between calibration points and the origin may use line segment calibration curves for each single component analyte. This technique may be used only if the r value (coefficient of determination) from the linear regression calculation is >0.975 for all three points for each single component analyte.

8.3.7 Sample analysis may not proceed until a satisfactory calibration has been demonstrated.

8.3.8 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, a new calibration curve or calibration factor must be prepared for that parameter.

8.4 QUANTITATION OF ANALYSES

8.4.1 Analytes can be quantitated using either manual measurement of onscale chromatograms, with a modern electronic integrator, or with a laboratory data system. The analyst can use either peak height or peak area as the basis for quantitation. The use of manual integration is strongly discouraged.

8.4.2 If manual quantitation is used, all peaks used for calibration and for sample analysis must be onscale and give at least 20 percent deflection from baseline at maximum height. Guidance in the manual quantitation of peaks is given in the EPA MANUAL OF ANALYTICAL METHODS FOR THE ANALYSIS OF PESTICIDES IN HUMANS AND ENVIRONMENTAL SAMPLES, EPA-600/8-80-038, or in the FDA Pesticide Analytical Manual.

8.4.3 If electronic integration is used, it is the responsibility of the analyst to be sure that the integration parameters are set properly and that off-scale chromatograms are within the dynamic range of the device. The analyst should also check for data flags that indicate improper quantitation of peaks prior to reporting data to the EPA. In addition, the peak width of identified analytes must not be more than 2.0 times the width of the high concentration calibration peak(s) for the same analyte.

8.4.4 The detector response (peak area or peak height) to all of the analytes must lie between the response of the low and high concentrations in the three-point initial calibration in order to be quantitated.

8.4.5 The concentration of the surrogate and of the single component analytes are calculated using the following equations:

8.4.5.1 Water

$$\text{concentration} \quad \mu g/L = \frac{(A_x)(V_t)}{(CF)(V_i)(V_x)} \qquad (5.10)$$

Where:

A_x = Response for the parameter to be measured.

CF = Calibration factor for the external standard.

V_t = Volume of total extract (μL) (take into account any dilution).

V_i = Volume of extract injected (μL).

V_x = Volume of water extracted (mL).

8.4.5.2 Sediment/Soil

$$\text{Concentration} \quad \mu g/kg = \frac{(A_x)\ (V_t)}{(CF)(V_i)(W_s)(D)} \qquad (5.10)$$

(Dry weight basis)

Where:

A_x, CF, V_i = same as given above in 5.3.4.1

$$D = \frac{100 - \text{percent weight loss}}{100} \quad \text{(percent weight loss from Section 3.3)}$$

W_s = Weight of sample extracted (g)

8.5 FLOW SCHEME

8.5.1 A flow scheme for the analysis of samples by this procedure are given in Figure 1.

8.6 SAMPLE CHROMATOGRAMS

8.6.1 Sample chromatograms of mixtures containing all single component analytes and of all multi-component analytes are presented in Figures 2-23.

8.7 METHOD DETECTION LIMIT

8.7.1 Any method is dependent on the complexity of the sample matrix analyzed, but this procedure can be used to determine all of the phenoxyacid analytes except 24-D (Table 3) to a detection limit of <5 ppb. If greater sensitivity is required, the remaining 9 mL of iso-octane extract can be blown down to 1 mL (3.3.2) and esterified. This concentrate can be used to give a method detection burst of 0.5 ppb.

9.0 QUALITY CONTROL

9.1 Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed to demonstrate that all glassware and reagents are interference-free. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware; these contaminants lead to discrete artifacts, and/or elevated baselines, in gas chromatograms. Interferences by phthalate esters especially can pose a major problem in pesticide analysis when using the electron capture detector. Common flexible plastics contain varying amounts of phthalates which are easily extracted during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

9.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. It is suggested that the response of the external standards be plotted daily as a quality control check. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as GC/MS should be used.

9.3 Waste samples spiked with selected analytes must be analyzed for at least 10% of the samples to validate the accuracy of the analysis. The results of the recovery of spiked analytes must be reported with sample data.

9.4 At the option of the I.T.D., the requirement for spiking at least 10% of the samples with selected herbicides may be replaced with a requirement for analyzing a matrix spike/matrix spike duplicate (MS/MSD) pair for every 20 samples analyzed.

9.5 The MS/MSD pair are prepared by spiking duplicate sample aliquots with the particular matrix spiking solutions described below. The MS/MSD pair as well as the unspiked sample are analyzed by the procedures described in this protocol. The recoveries of the matrix spike compounds are reported with the sample data using the formula below.

$$\text{Matrix spike recovery} = \frac{SSR-SR}{SA} \times 100$$

SSR = Sample spike results
SR = Sample result
SA = Spike added

9.5.1 The apolar MS/MSD samples are each spiked with two solutions. One for organochlorine compounds and the other for organophosphates. The spiking solution for organochlorines is the same one as is used in the CLP analysis of organochlorine pesticides and is listed below.

Pesticide	µg/1.0 mL
gamma-BHC	0.5
Heptachlor	0.5
Aldrin	0.5
Dieldrin	1.0
Endrin	1.0
4,4'-DDT	1.0

The spiking solution for organophosphate pesticides is listed below.

Pesticide	µg/1.0 mL
Chlorpyriophos	100
Fenthion	100
Malathion	100
Parathion, ethyl	100
Carbofenthion	100

The solutions are prepared in acetone and must be allowed to equilibrate at room temperature before they are spiked.

9.5.2 The phenoxyacid MS/MSD samples are spiked with the mixture listed below.

Herbicide	µg/1.0 mL
2,4-D	0.5
2,4,5-T	0.5

The solution is prepared in acetone and must be allowed to equilibrate at room temperature before it is spiked.

9.6 It is critical that analysts become proficient with capillary GC analysis before using this method to generate quantitative results.

9.7 Store stock solutions of standards at 4°C and protect from light. All such solutions must be checked frequently for signs of degradation or evaporation. Organophosphorous standards are particularly prone to hydrolysis during storage.

10.0 REFERENCES

10.1 *Statement of Work - GC Methods for Environment Samples, Pesticides, PCP's (proposed)*, Prepared for J. Fisk, Office of Remedial and Emergency Response, USEPA, by P. Marsden and D. Bottrell.

10.2 *Single-Laboratory Validation of EPA Method 8150 for the Analysis of Chlorinated Herbicides in Hazardous Waste*, EPA 600/4-85-060, prepared for D.F. Gurka, QAD, EMSL-LV, by F. Shore, E.N. Amick, and S.T. Pan.

10.3 *Single Laboratory Validation of EPA Method 8140 for the Analysis of Organophosphorous Pesticides in Hazardous Waste (in manuscript)*, prepared for D. Betowski, QAD, EMSL-LV, by V. Taylor, D. Hickey, and P. Marsden.

10.4 *Methods for Organic Chemical Analysis of Municipal and Industrial Waste Water*, EPA 600/4-82-057, by J.E. Longbottom and J.J. Lichtenberg.

TABLE 1

APOLAR ORGANOCHLORINE
PARAMETERS OF THE CONSOLIDATED METHOD

COMPOUND	METHOD	RETENTION TIME DB-5	SPB-608	DB-608
Aldrin	608,617	19.77	18.33	22.66
Aroclor 1016	608,617	multiple	multiple	multiple
Aroclor 1221	608,617	multiple	multiple	multiple
Aroclor 1232	608,617	multiple	multiple	multiple
Aroclor 1242	608,617	multiple	multiple	multiple
Aroclor 1248	608,617	multiple	multiple	multiple
Aroclor 1254	608,617	multiple	multiple	multiple
Aroclor 1260	608,617	multiple	multiple	multiple
BHC,alpha	608,617	13.77	13.70	18.48
BHC,beta	608,617	14.74	15.04	20.41
BHC,gamma	608,617	15.01	15.22	20.09
BHC,delta	608,617	15.93	17.15	21.86
Captan	617	22.03	24.24	nd
Carbophenthion	617,622	28.44	26.59	30.43
Chlordane	608,617	multiple	multiple	multiple
Chlorobenzylate	608.1	26.49	26.03	25.35
DDD	608,617	26.99	26.79	29.17
DDE	608,617	24.70	24.16	27.10
DDT	608,617	29.01	28.75	30.33
Dibutylchlorendate	no	34.20	32.61	33.47
Dichloran	617	14.31	14.80	19.73
Dieldrin	608,617	24.88	24.35	27.34
Endosulfan I	608,617	23.54	22.81	26.17
Endosulfan II	608,617	26.49	27.15	29.38
Endosulfan sulfate	608,617	28.77	29.41	31.21
Endrin	608,617	26.02	26.11	28.69
Endrin Aldehyde	608,617	27.48	28.82	31.21
Endrin ketone	no	31.25	33.27	31.51
Heptachlor	608,617	18.14	16.87	21.38
Heptachlor epoxide	608,617	21.69	21.01	24.86
Hexabromobenzene	no	31.85	31.54	34.79
Hexachlorobenzene	no	14.24	13.37	nd
Isodrin	617	21.19	20.33	24.36
Methoxychlor	617	32.17	33.37	33.46
Mirex	no	34.49	33.59	33.68
Nitrofen	608.1,617	25.99	26.35	27.66
PCNB	617	15.24	14.78	19.50
Toxaphene		multiple	multiple	multiple
Trifluralin		12.95	11.01	14.83

RELATED COMPOUNDS

COMPOUND	METHOD	DB-5	SPB-608	
Captofol	no	31.26	26.83	
Chloroneb	608.1	10.46	10.67	
Chloropropylate	608.1	nd	nd	
DBCP	608.1	5.91	5.96	7.6
Dicofol	617	32.35	32.76	
Etridazole	608.1	9.82	9.76	
Kepone	no	28.04	26.28	
Perthane (Ethylan)	no	26.23	26.09	
Propachlor	617	nd	nd	
Strobane	608,617	multiple	multiple	multiple
Diallate(cis,trans)	no	13.57,13.91	12.89,13.20	

nd = not determined

TABLE 2

APOLAR ORGANOPHOSPHOROUS
PARAMETERS OF THE CONSOLIDATED METHOD

COMPOUND	METHOD	RETENTION TIME DB-5	SPB-608
Azinphos ethyl	no	39.04	38.49
Azinphos methyl	614,622	38.34	38.04
Carbophenthion	617,622	25.25	35.10
Chlorfenvinphos	no	33.57	31.86
Chlorpyrophos	622	31.17	26.88
Coumophos	622	39.83	38.87
Demeton(mixed)	614,622	18.31,20.96	15.90,18.84
Diazinon	614,622,7	24.27	20.00
Dichlovos	622	9.63	7.91
Dicrotophos		15.23	19.12
Dimethoate		20.64	20.18
Dioxathion		39.93	33.17
Disulfoton	614,622	23.71	19.96
EPN		37.80	36.71
Ethion	614,701	36.17	34.79
Famphur		36.43	35.93
Fensulfothion	622	35.83	35.20
Fenthion	622	31.83	29.45
HMPA		10.69	9.23
Leptophos		38.47	37.25
Malathion	614,701	31.72	28.78
Mevinphos	622	14.19	12.88
Monocrotophos		20.04	20.11
Naled	622	19.01	17.40
Parathion, ethyl	614,701	31.85	27.62
Parathion, methyl	614,622,7	31.83	23.71
Phorate	622	19.94	17.52
Phosmet		37.56	37.20
Phosphamidon		27.05	24.46
Sulfotepp		20.11	18.02
TEPP		6.44	5.12
Terbuphos		22.63	18.81
Tetrachlorovinphos		34.65	32.99
TOCP		38.79	37.71
Trichlorofon		11.91	nd
Trimethyl phosphate		2.35	nd

RELATED COMPOUNDS

COMPOUND	METHOD	DB-5	SPB-608
Bolstar	622	36.74	nd
Chlorpyrophos.me	622	nd	nd
Crotoxyphos	no	34.06	33.07
Dichlorfenthion	701	9.63	7.91
Ethoprop	622	18.62	16.48
Merphos	622	nd	26.82
Methyl trithion	701	nd	no
Ronnel	no	29.23	22.98
Tokuthion	no	34.67	no
Trichloronate	no	32.19	nd

TABLE 3

PHENOXYACID
ANALYTES OF CONSOLIDATED METHOD

COMPOUND	METHOD	DB-5	SPB-608
Dinoseb	615	30.28	26.25
2,4-D	615	20.84	22.91
2,4,5-T	615	26.95	29.13
2,4,5-TP	615	25.73	29.83
RELATED COMPOUNDS			
Dalapon	615		
2,4-DB	615	29.7	32.15
Dicamba	615		
Dichlorprop	615		
MCPA	615		
MCPP	615		

TABLE 4

RECOVERY OF SINGLE COMPONENT HALOGENATED PESTICIDES (50 ng/L)

COMPOUND	DB-5 RECOVERY (%)	rsd	SPB-608 RECOVERY (%)	rsd
Aldrin	82.2	5.1	75.7	10.3
BHC,alpha	105.9	7.9	108.7	5.4
BHC,beta	94.2	9.1	99.9	6.5
BHC,gamma	109.9	3.8	103.3	5.7
BHC,delta	* 30.4	48	* 27.0	16
Captan	nd		nd	
Carbophenthion	* 185.2	8	*	
Chlorobenzylate	118.2	12	86.5	8.8
DDD	117.2	8.5	113.2	10.6
DDE	82.1	32	89.0	25
DDT	97.3	18	89.1	8.9
Diallate	nd		nd	
Dichloran	23.4	26	28.1	13
Dieldrin	93.7	16	102.8	9.3
Endosulfan I	81.6	16	83.8	13
Endosulfan II	63.7	34	74.4	24
Endosulfan SO4	* 38.3		* 14.5	25
Endrin	97.2	22	100.6	16
Endrin Aldehyde	* 22.2		*	
Endrin ketone	* 14.1	23	*	
Heptachlor	* 59.1	28	* 60.4	28
Heptachlor epoxide	* 468.3		85.1	4.6
Hexachlorobenzene	nd		nd	
Isodrin	54.9	21	59.2	17
Methoxychlor	104.9	12	106.6	3.9
Mirex	90.5	9.8	108.5	7.1
Nitrofen	90.3	11	115.0	6.5
PCNB	97.5	14	93.3	16
Trifluralin	111.3	5.5	123.8	2.9

Values marked with a (*) had coeluting peaks
nd = not determined

TABLE 5

RECOVERY OF PHOSPHATE PESTICDES SPIKED AT 50 PPB

compound	recovery	r.s.d.
Azinphos ethyl	77.0	8.9%
Azinphos methyl	83.1	4.9%
Carbophenthion	136.6	15.8%
Chlorpyrophos	84.1	4.8%
Coumophos	73.0	9.3%
Diazinon	86.9	4.6%
Dichlorvos	80.6	4.5%
Dicrotophos	95.8	5.8%
Dimethoate	42.5	31.4%
Dioxathion	79.6	7.2%
EPN	81.8	6.0%
Ethion	82.0	5.4%
Famphur	62.8	14.5%
HMPA	120.2	4.4%
Leptophos	77.2	8.9%
Malathion	89.8	5.9%
Parathion, ethyl	82.6	7.4%
Parathion, methyl	82.0	5.6%
Phorate	97.0	5.0%
Sulfotepp	100.7	5.2%
TEPP	82.0	18.2%
Terbuphos	87.3	4.5%
Tetrachlorovinphos	88.3	11.0%
TOCP	81.7	8.0%
Trichlorofon	40.4	27.9%
Trimethyl phosphate	25.6	15.1%

TABLE 6

RECOVERY OF PHENOXYACID HERBICIDES SPIKED AT 10 PPB

COMPOUND	PERCENT RECOVERY	r.s.d.
Dinoseb	58	9.8%
2,4-D	92	5.0%
2,4,5-T	69	9.1%
2,4,5-TP	60	7.6%
2,4-DB	86	9.5%

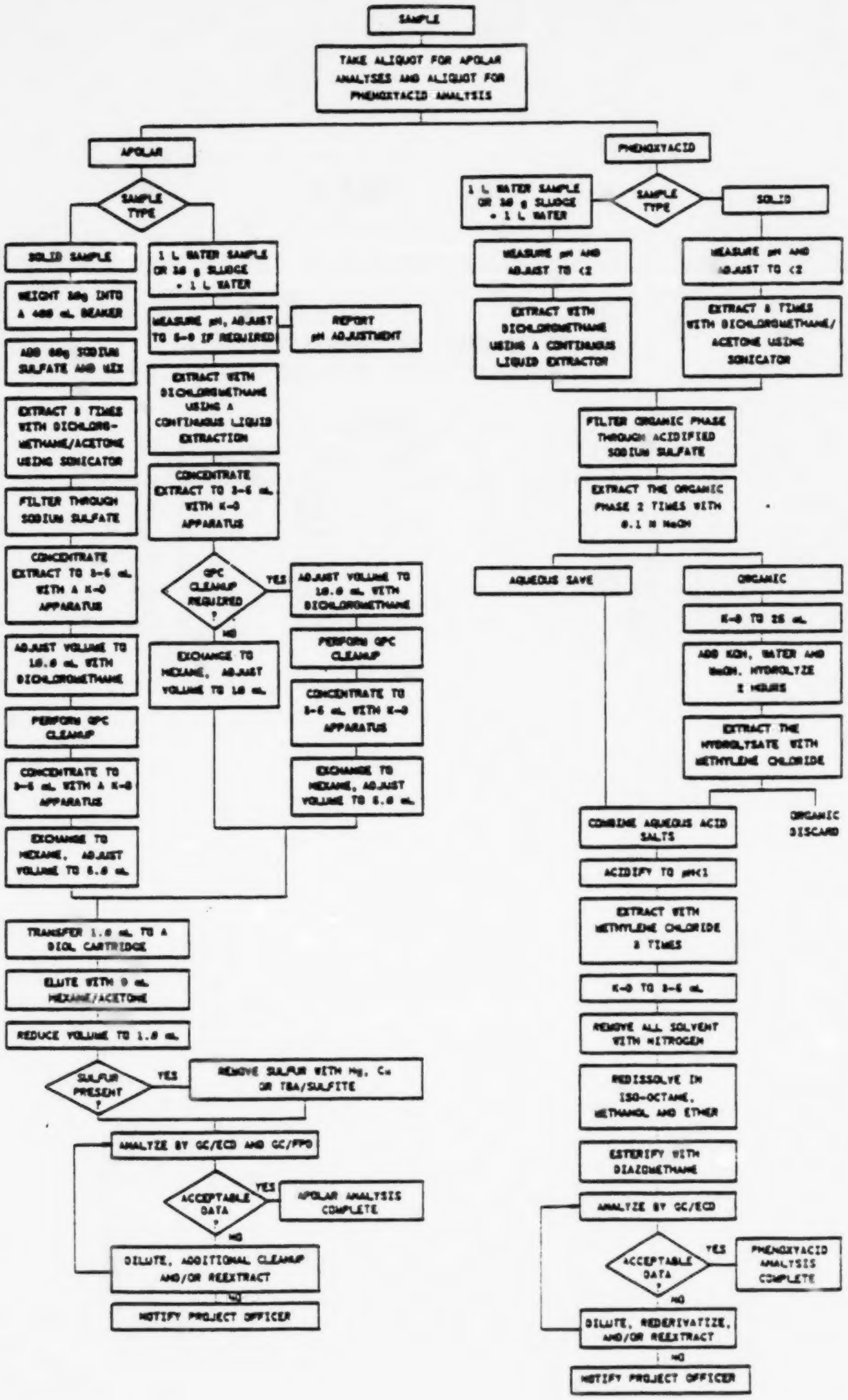
SAMPLE
TAKE ALIQUOT FOR APOLAR ANALYSES AND ALIQUOT FOR PHENOXYACID ANALYSIS
APOLAR
SAMPLE TYPE
SOLID SAMPLE
WEIGHT 30g INTO A 400 mL BEAKER
ADD 60g SODIUM SULFATE AND MIX
EXTRACT 3 TIMES WITH DICHLOROMETHANE/ACETONE USING SONICATOR
FILTER THROUGH SODIUM SULFATE
CONCENTRATE EXTRACT TO 3-6 mL WITH A K-D APPARATUS
ADJUST VOLUME TO 10.0 mL WITH DICHLOROMETHANE
PERFORM GPC CLEANUP
CONCENTRATE TO 3-6 mL WITH A K-D APPARATUS
EXCHANGE TO HEXANE, ADJUST VOLUME TO 5.0 mL
1 L WATER SAMPLE OR 30 g SLUDGE + 1 L WATER
MEASURE pH, ADJUST TO 5-9 IF REQUIRED
REPORT pH ADJUSTMENT
EXTRACT WITH DICHLOROMETHANE USING A CONTINUOUS LIQUID EXTRACTION
CONCENTRATE EXTRACT TO 3-6 mL WITH K-D APPARATUS
GPC CLEANUP REQUIRED ?
YES
NO
ADJUST VOLUME TO 10.0 mL WITH DICHLOROMETHANE
PERFORM GPC CLEANUP
CONCENTRATE TO 3-6 mL WITH K-D APPARATUS
EXCHANGE TO HEXANE, ADJUST VOLUME TO 5.0 mL
EXCHANGE TO HEXANE, ADJUST VOLUME TO 10 mL
TRANSFER 1.0 mL TO A DIOL CARTRIDGE
ELUTE WITH 9 mL HEXANE/ACETONE
REDUCE VOLUME TO 1.0 mL
SULFUR PRESENT ?
YES
REMOVE SULFUR WITH Hg, Cu OR TBA/SULFITE
ANALYZE BY GC/ECD AND GC/FPD
ACCEPTABLE DATA ?
YES
APOLAR ANALYSIS COMPLETE
NO
DILUTE, ADDITIONAL CLEANUP AND/OR REEXTRACT
NO
NOTIFY PROJECT OFFICER
PHENOXYACID
1 L WATER SAMPLE OR 30 g SLUDGE + 1 L WATER
SAMPLE TYPE
SOLID
MEASURE pH AND ADJUST TO <2
MEASURE pH AND ADJUST TO <2
EXTRACT WITH DICHLOROMETHANE USING A CONTINUOUS LIQUID EXTRACTOR
EXTRACT 3 TIMES WITH DICHLOROMETHANE/ACETONE USING SONICATOR
FILTER ORGANIC PHASE THROUGH ACIDIFIED SODIUM SULFATE
EXTRACT THE ORGANIC PHASE 2 TIMES WITH 0.1 N NaOH
AQUEOUS SAVE
ORGANIC
K-D TO 25 mL
ADD KOH, WATER AND MeOH, HYDROLYZE 2 HOURS
EXTRACT THE HYDROLYSATE WITH METHYLENE CHLORIDE
ORGANIC DISCARD
COMBINE AQUEOUS ACID SALTS
ACIDIFY TO pH<1
EXTRACT WITH METHYLENE CHLORIDE 3 TIMES
K-D TO 3-5 mL
REMOVE ALL SOLVENT WITH NITROGEN
REDISSOLVE IN ISO-OCTANE, METHANOL AND ETHER
ESTERIFY WITH DIAZOMETHANE
ANALYZE BY GC/ECD
ACCEPTABLE DATA ?
YES
PHENOXYACID ANALYSIS COMPLETE
NO
DILUTE, REDERIVATIZE, AND/OR REEXTRACT
NO
NOTIFY PROJECT OFFICER

Figure 1. Flow Scheme for the Analysis of Samples.

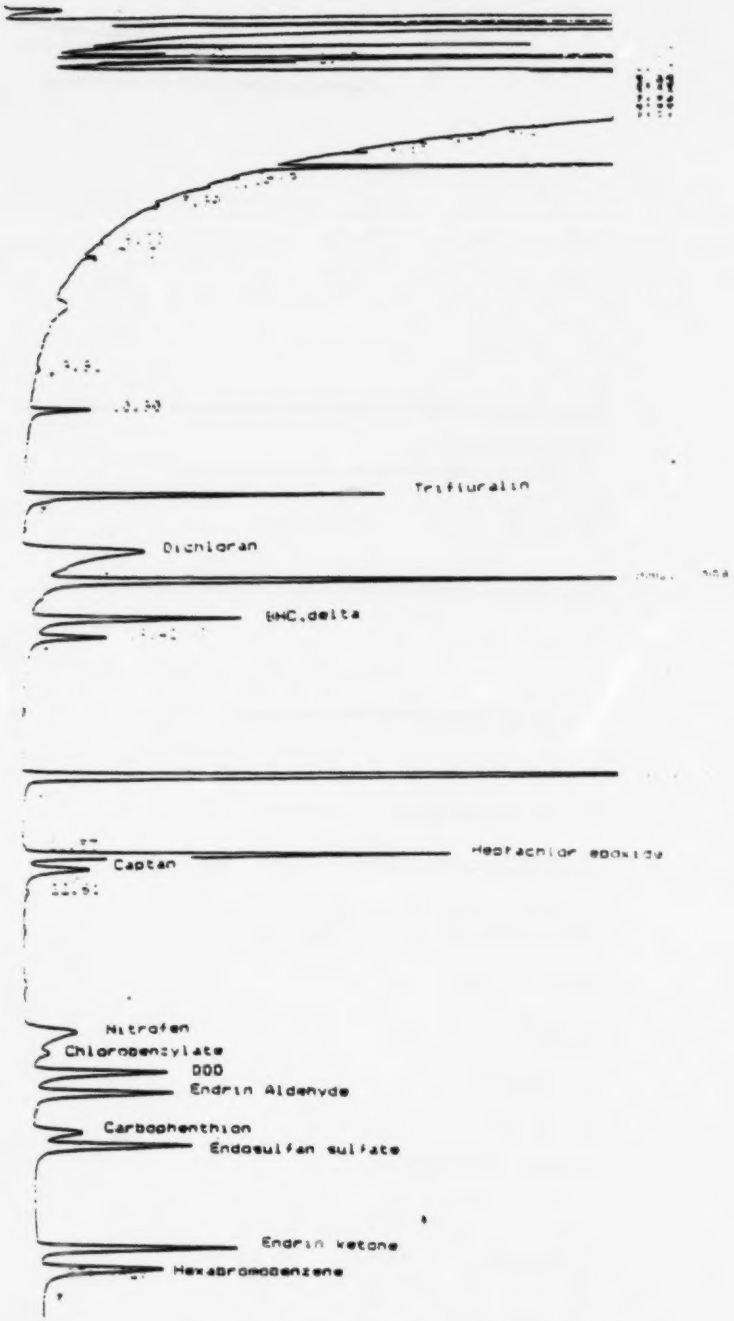

Figure 2A. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the DB-5.

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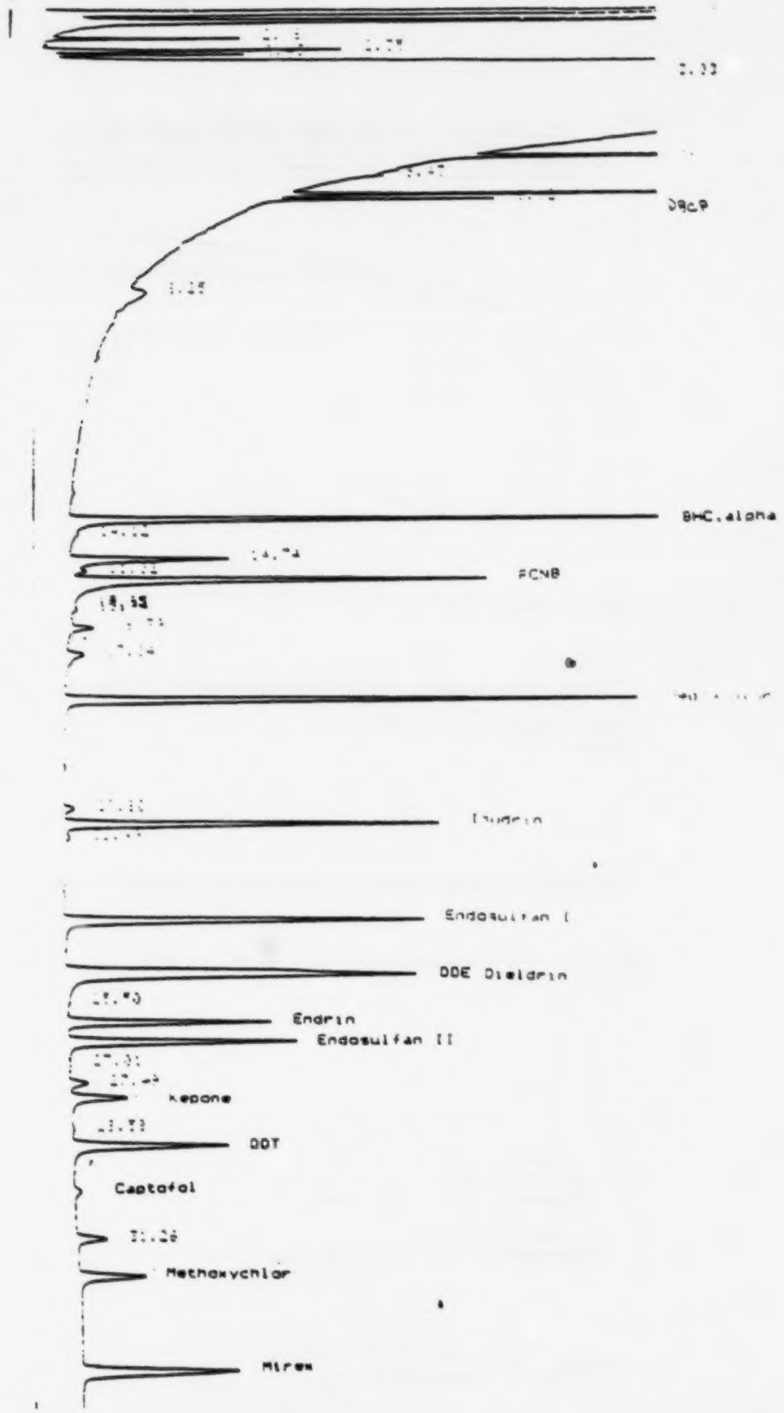

Figure 2B. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the DB-5.

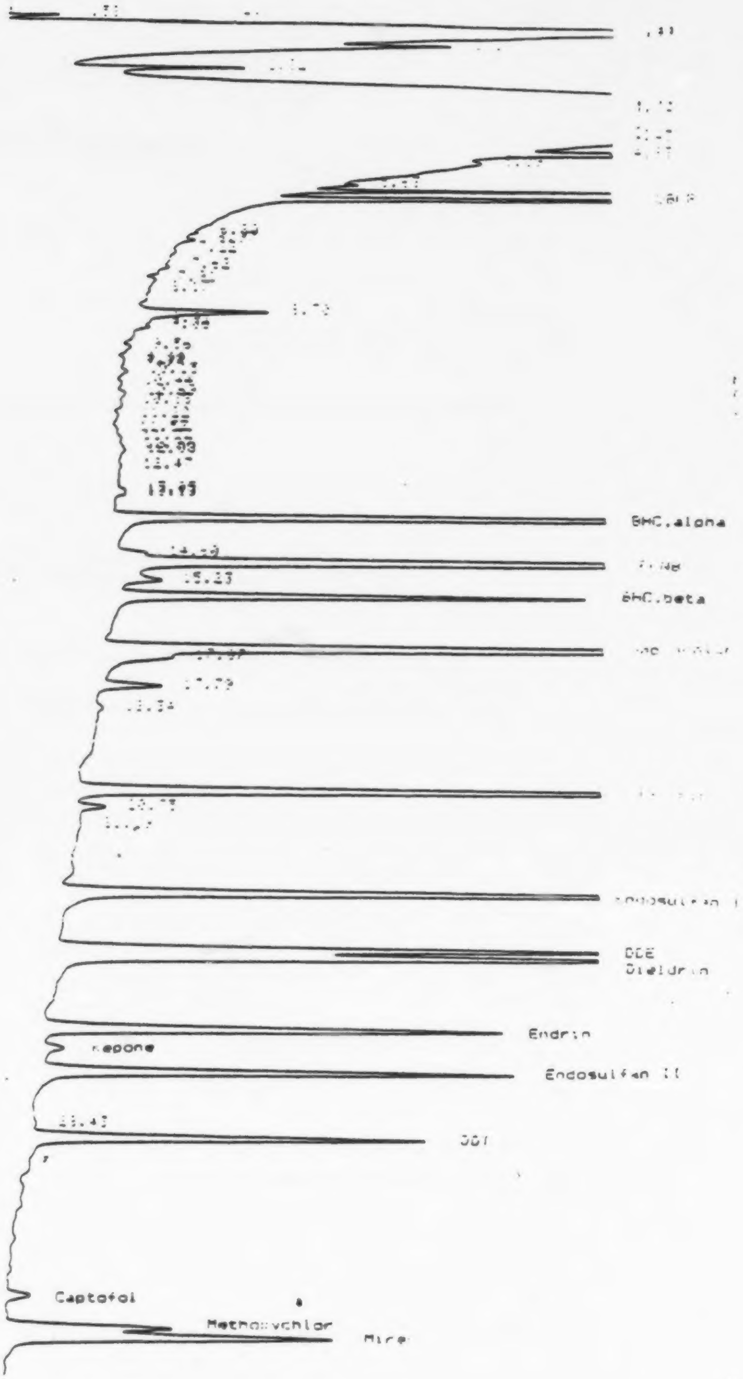

Figure 3A. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the SPB-608.

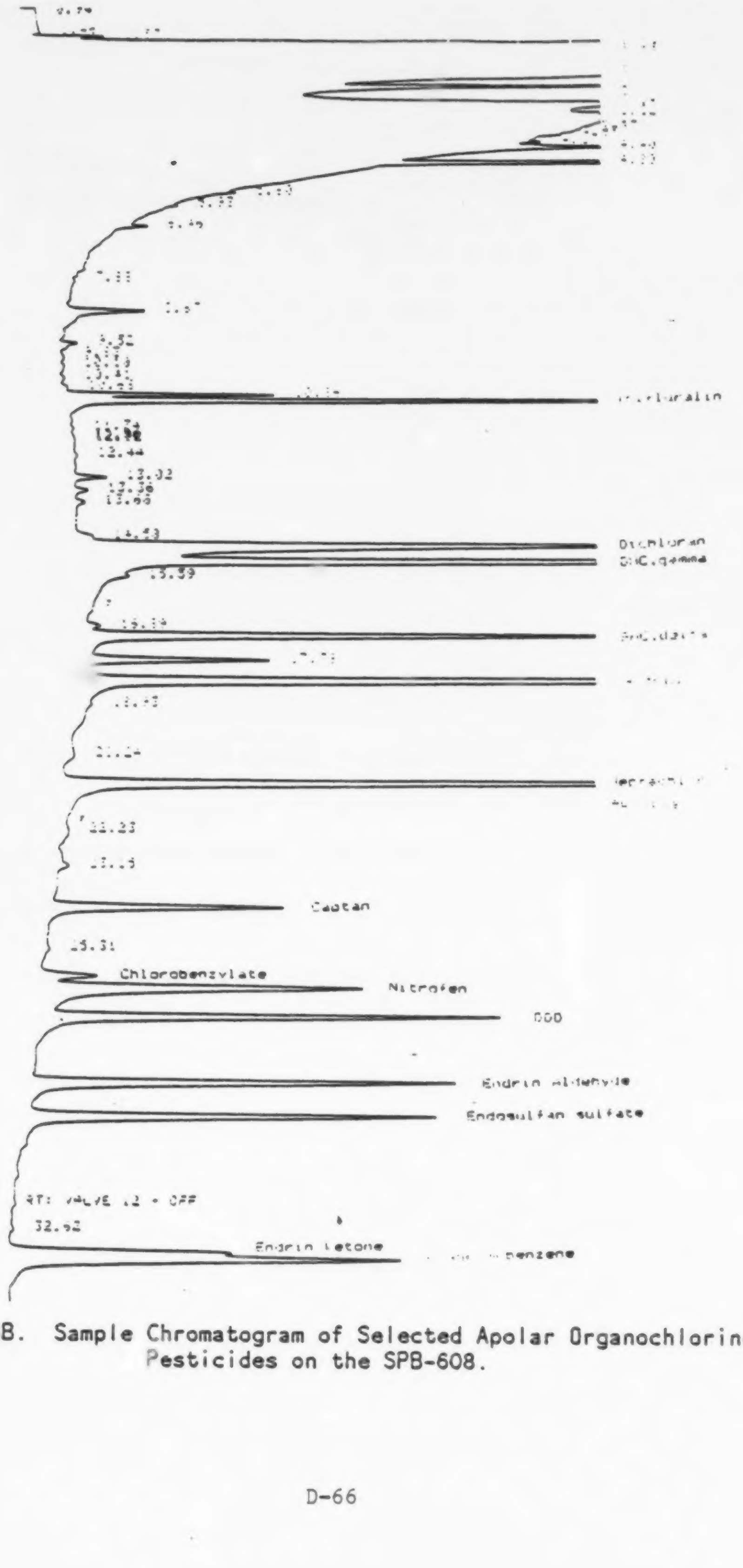

Figure 3B. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the SPB-608.

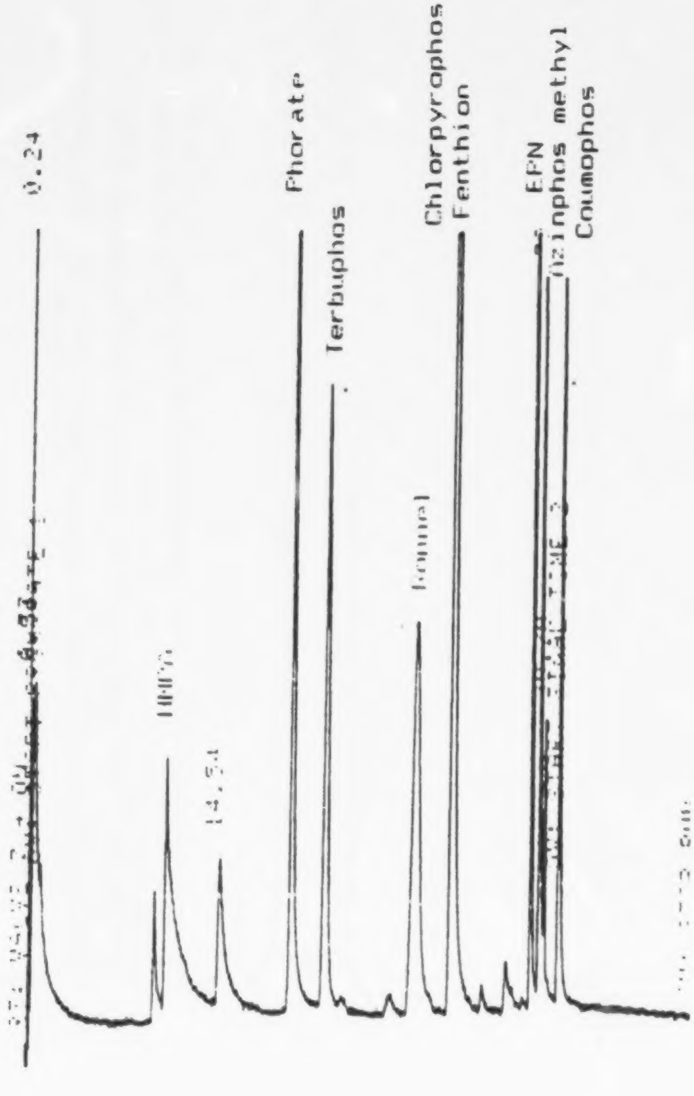

Figure 4A. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the DB-5.

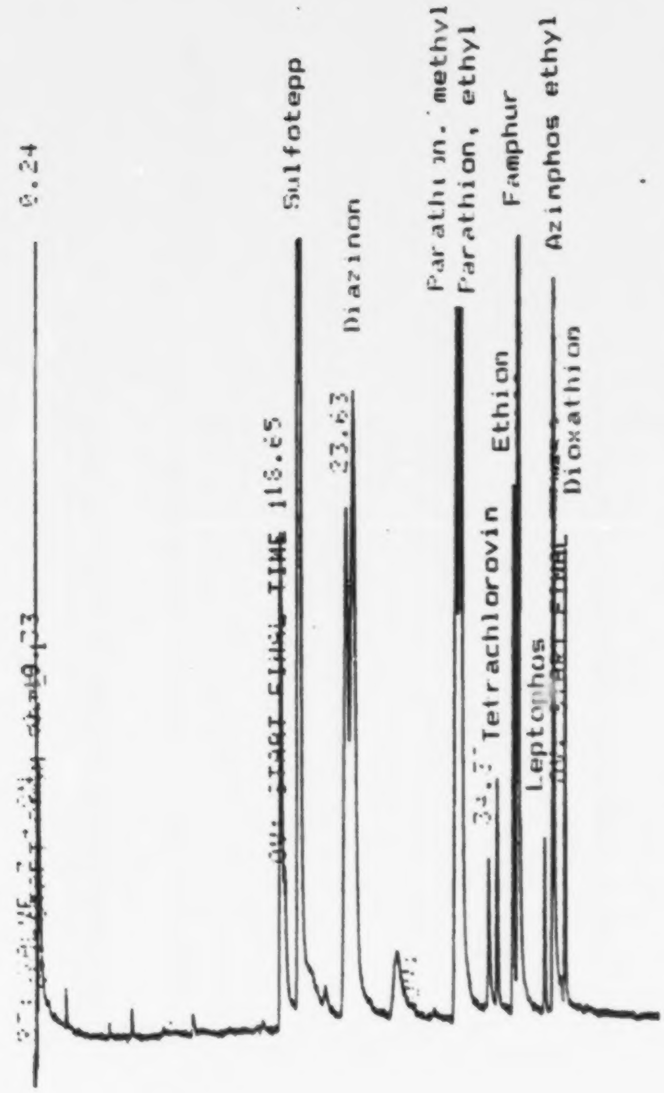

Figure 4B. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the DB-5.

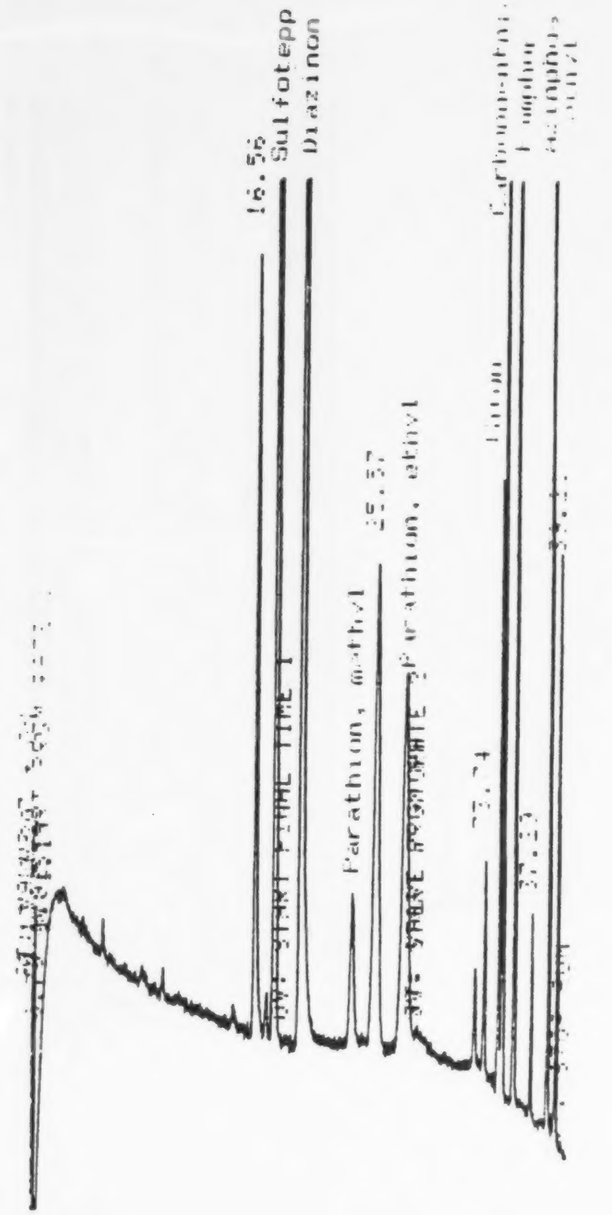

Figure 5A. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the SPB-608.

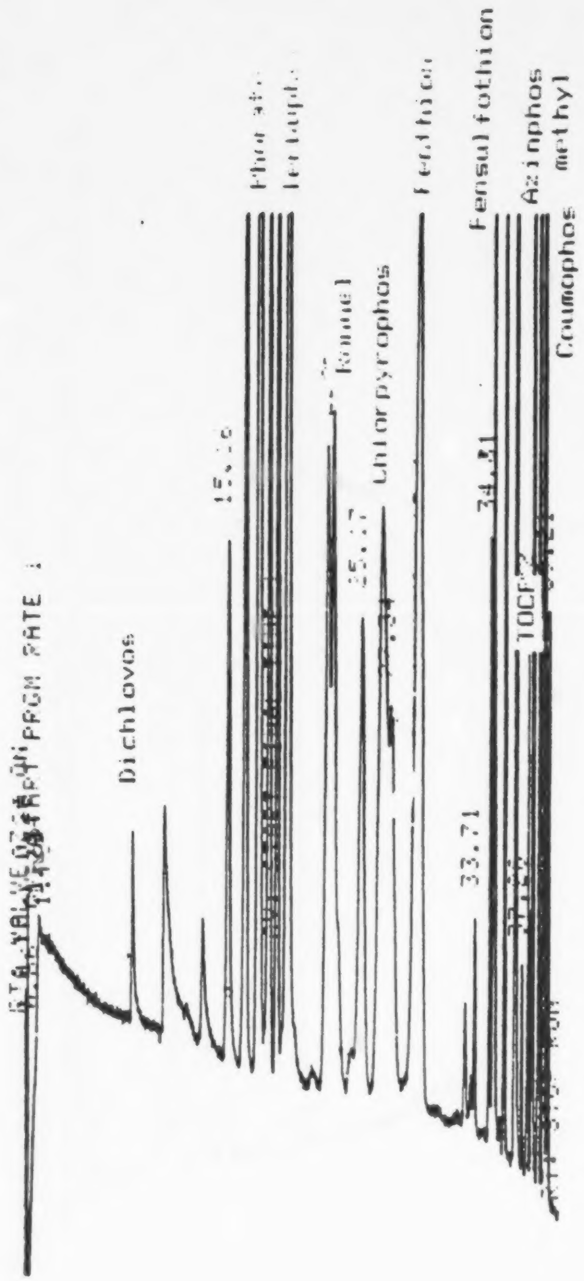

Figure 58. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the SPB-608.

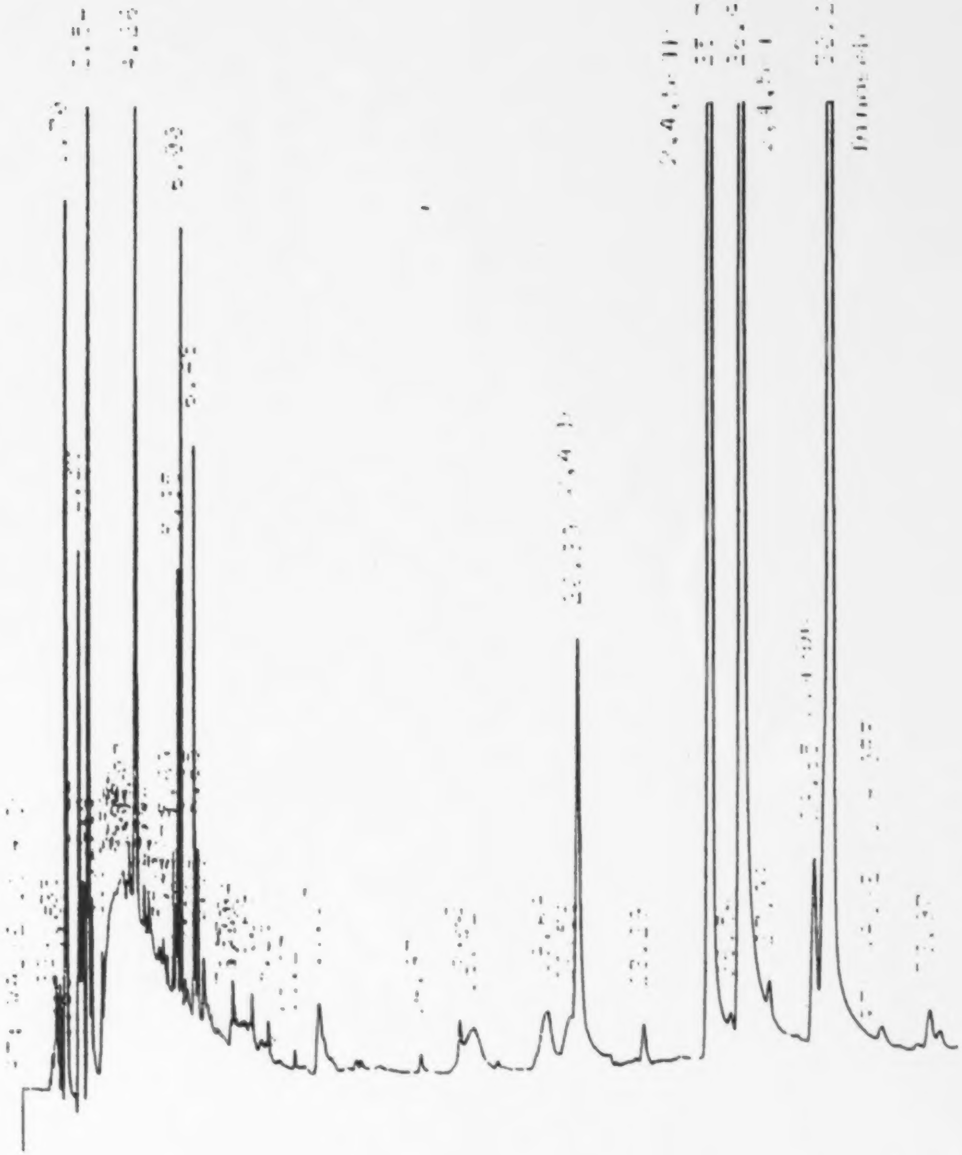

Figure 6. Sample Chromatogram of Phenoxyacids on the DB-5.

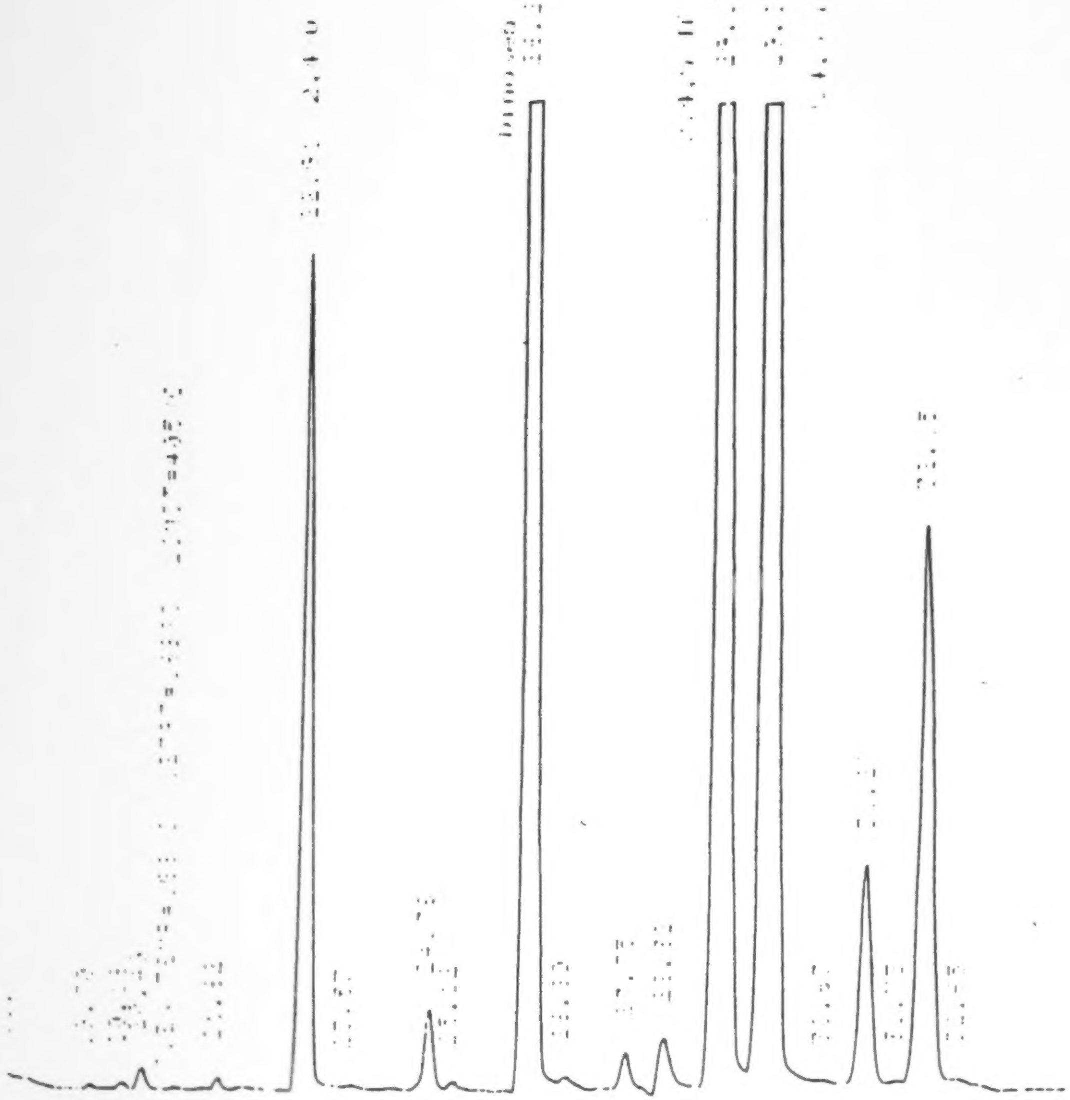

Figure 7. Sample Chromatogram of Phenoxyacids on the DB-608.

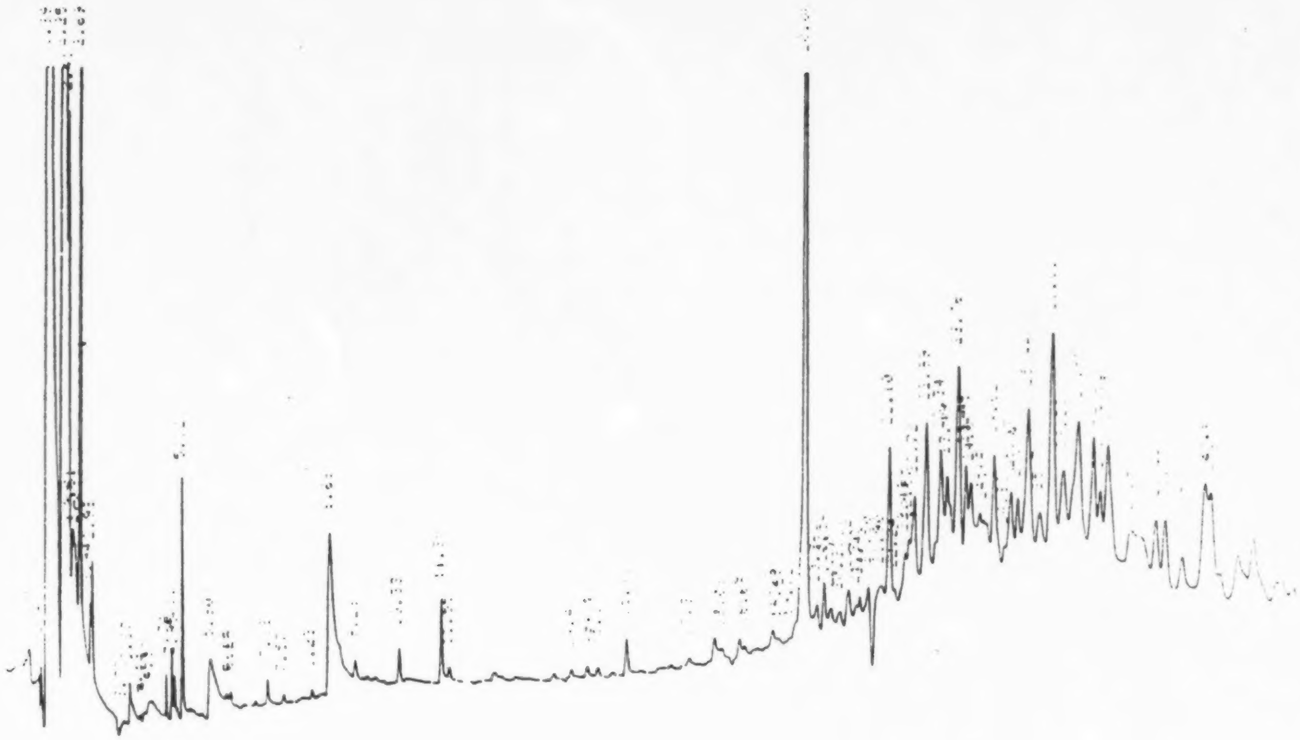

Figure 8. Toxaphene on the DB-5.

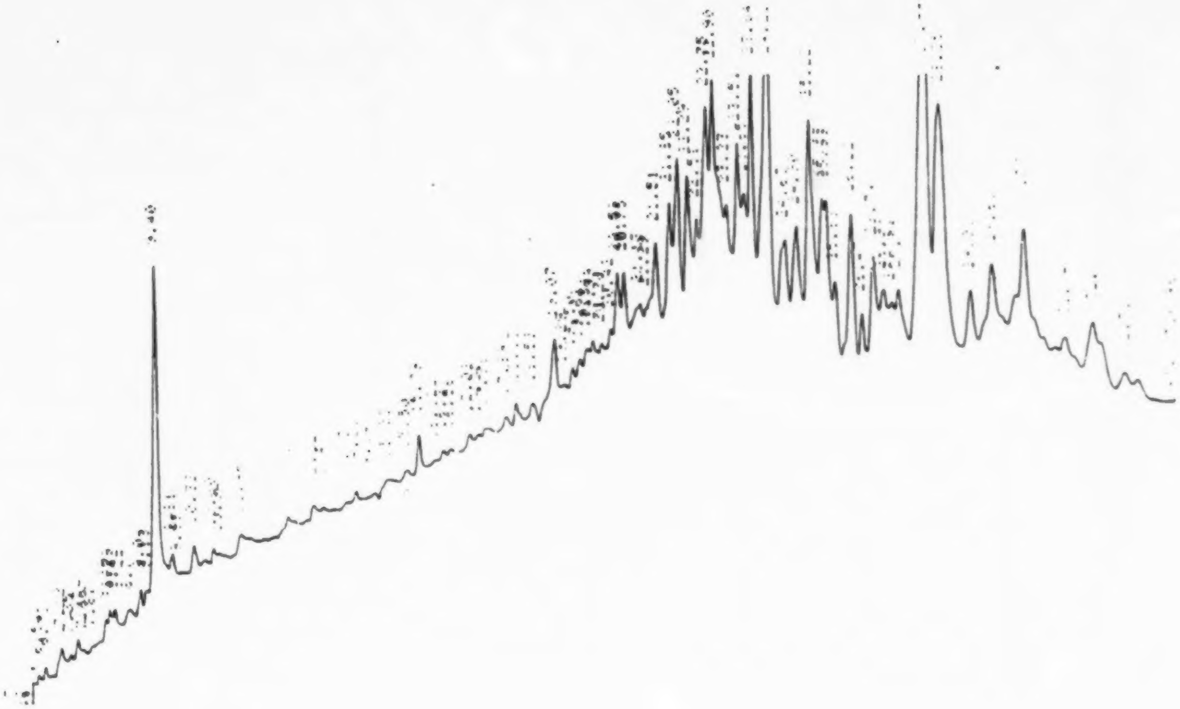

Figure 9. Toxaphene on the SPB-608.

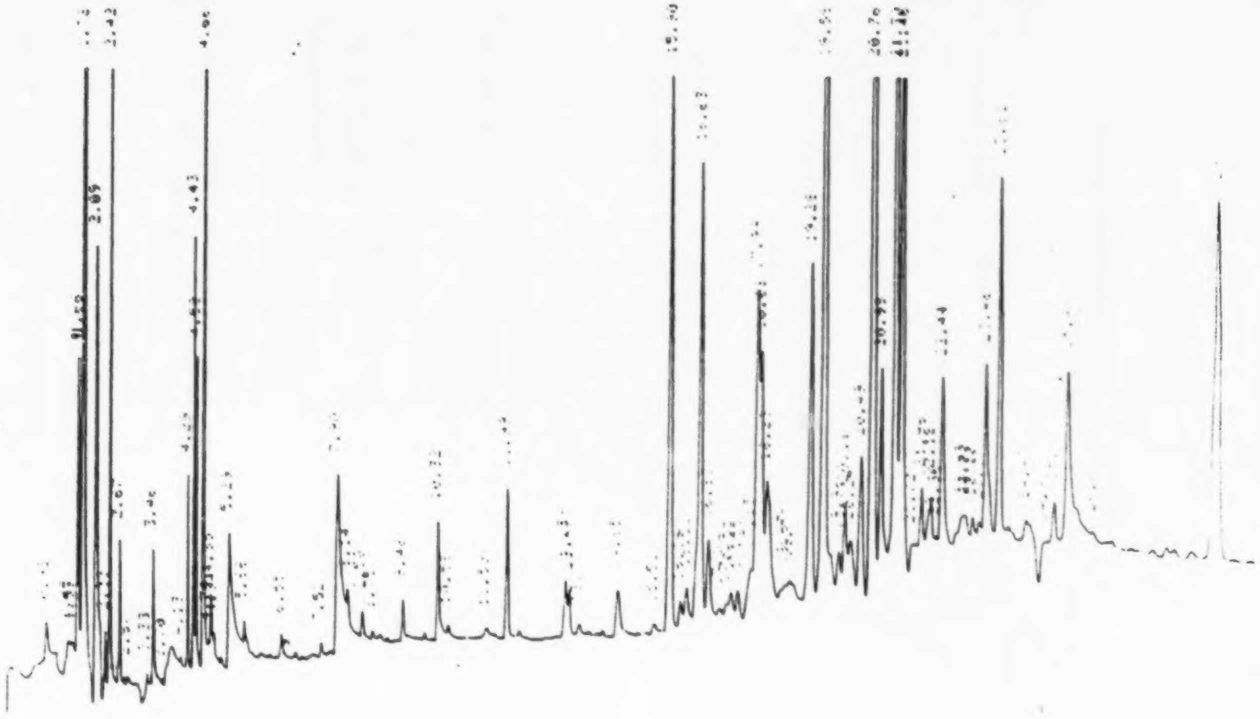

Figure 10. Chlordane on the DB-5.

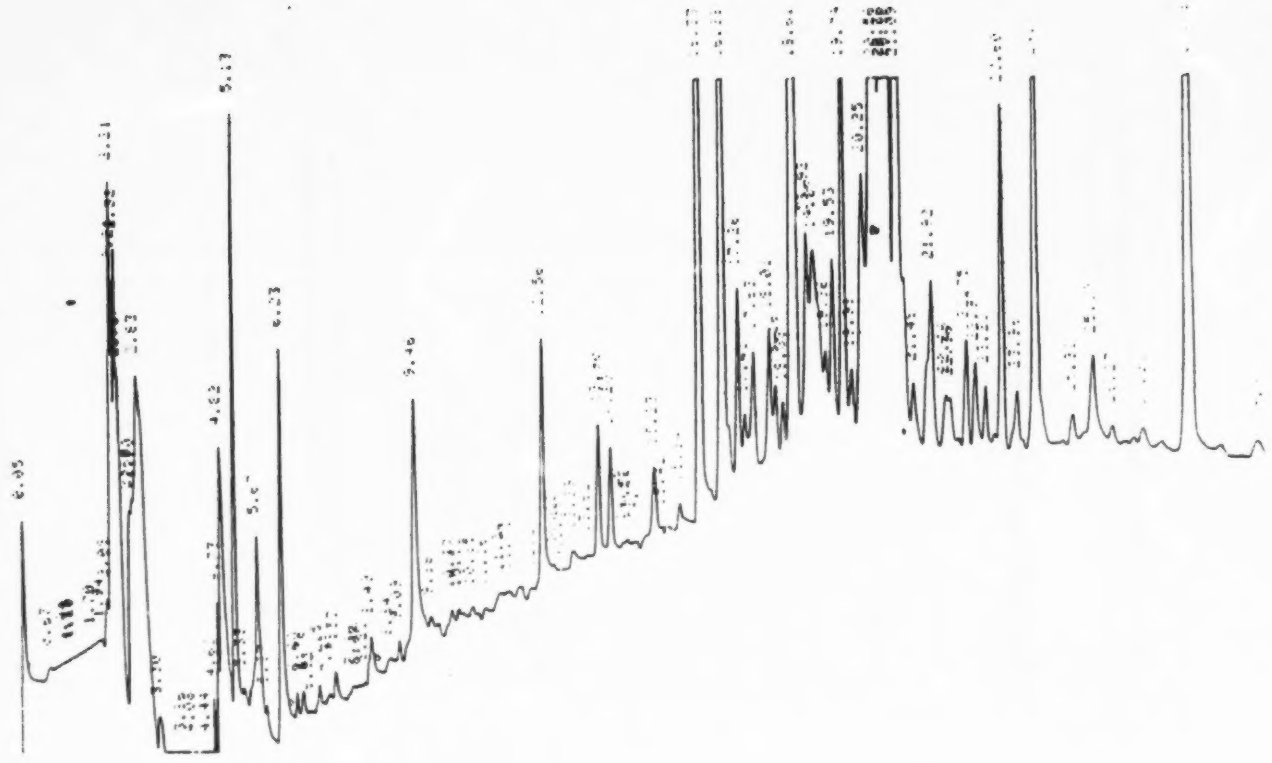

Figure 11. Chlordane on the SPB-608.

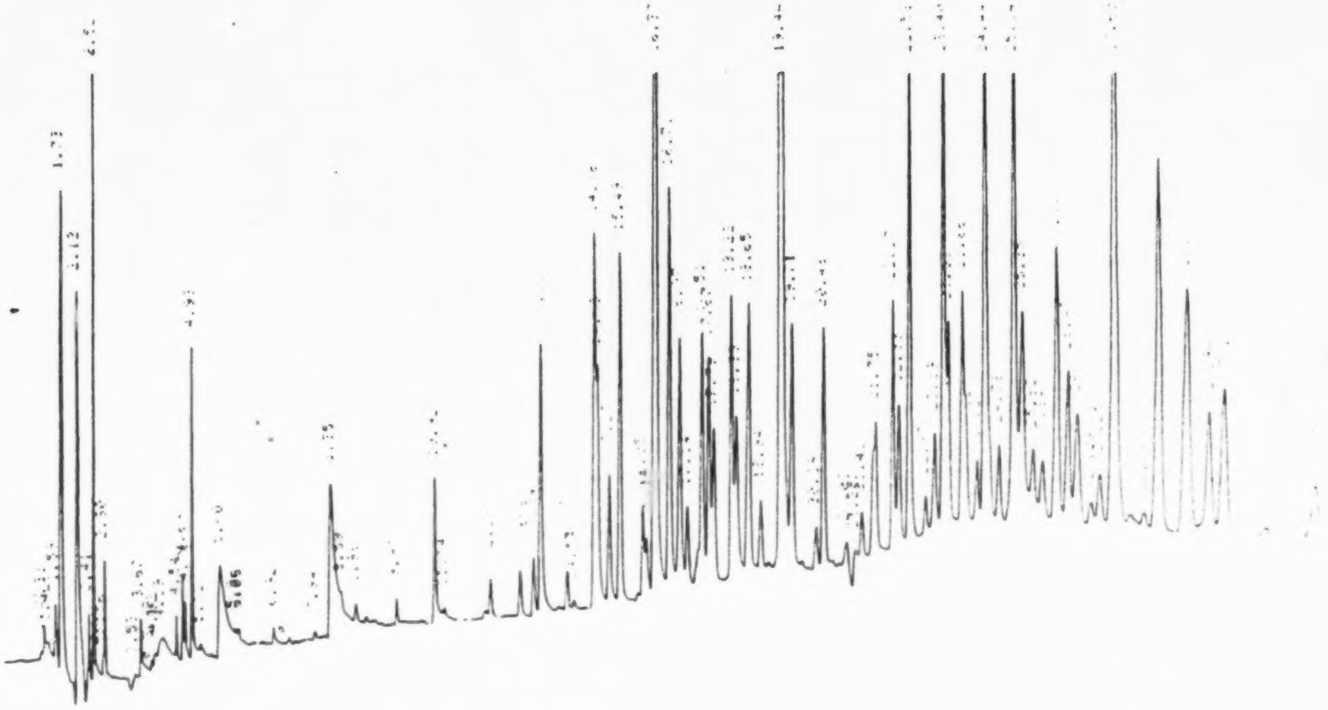

Figure 12. Aroclor 1016/1260 on the DB-5.

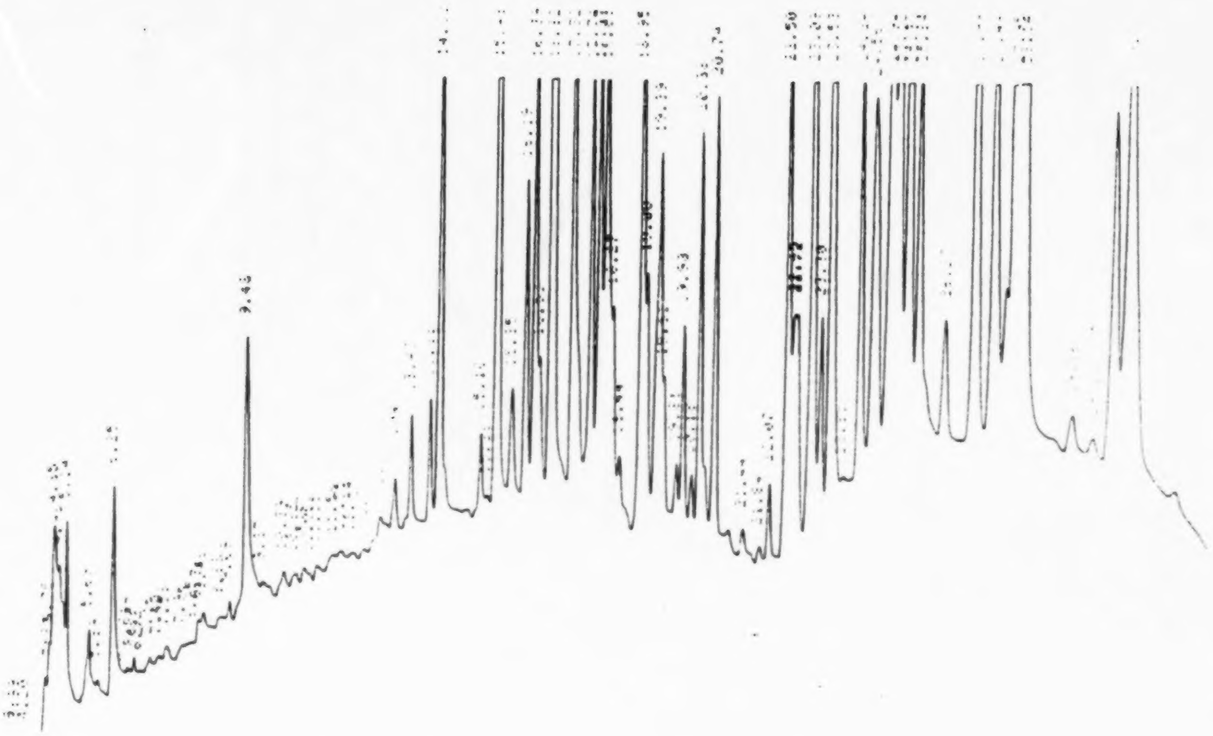

Figure 13. Aroclor 1016/1260 on the SPB-608.

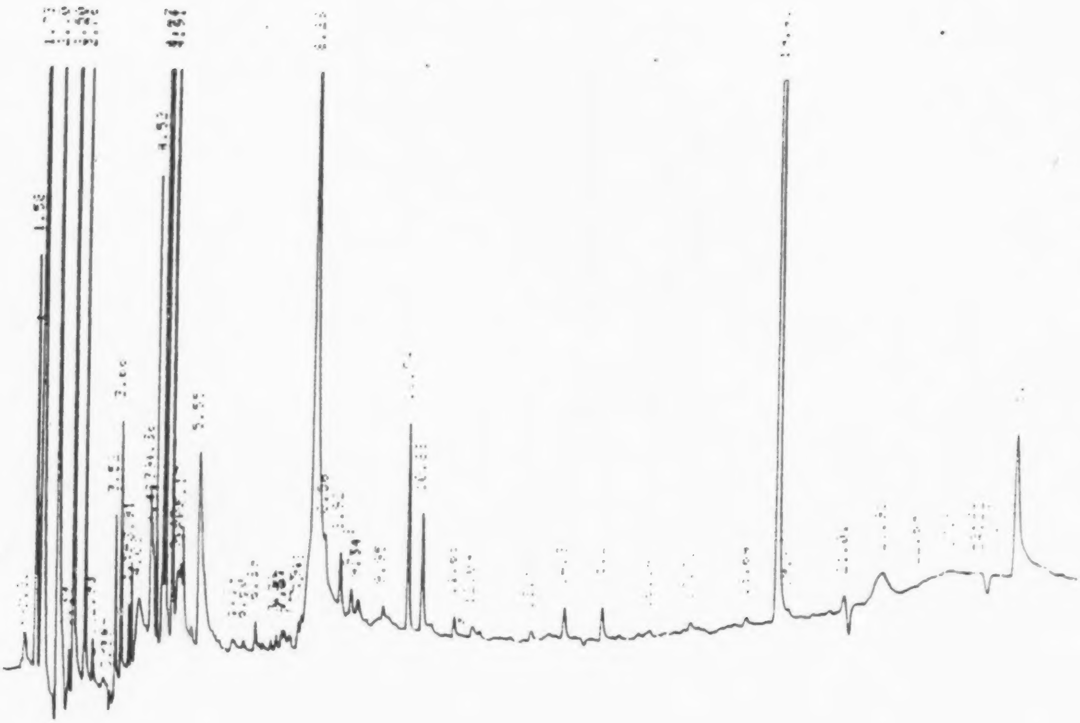

Figure 14. Aroclor 1221 on the DB-5.

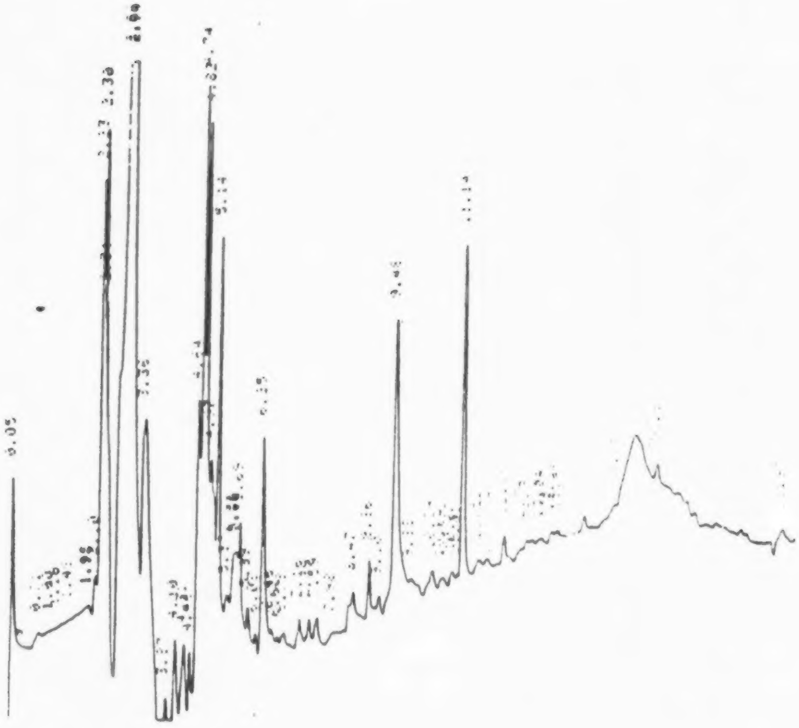

Figure 15. Aroclor 1221 on the SPB-608.

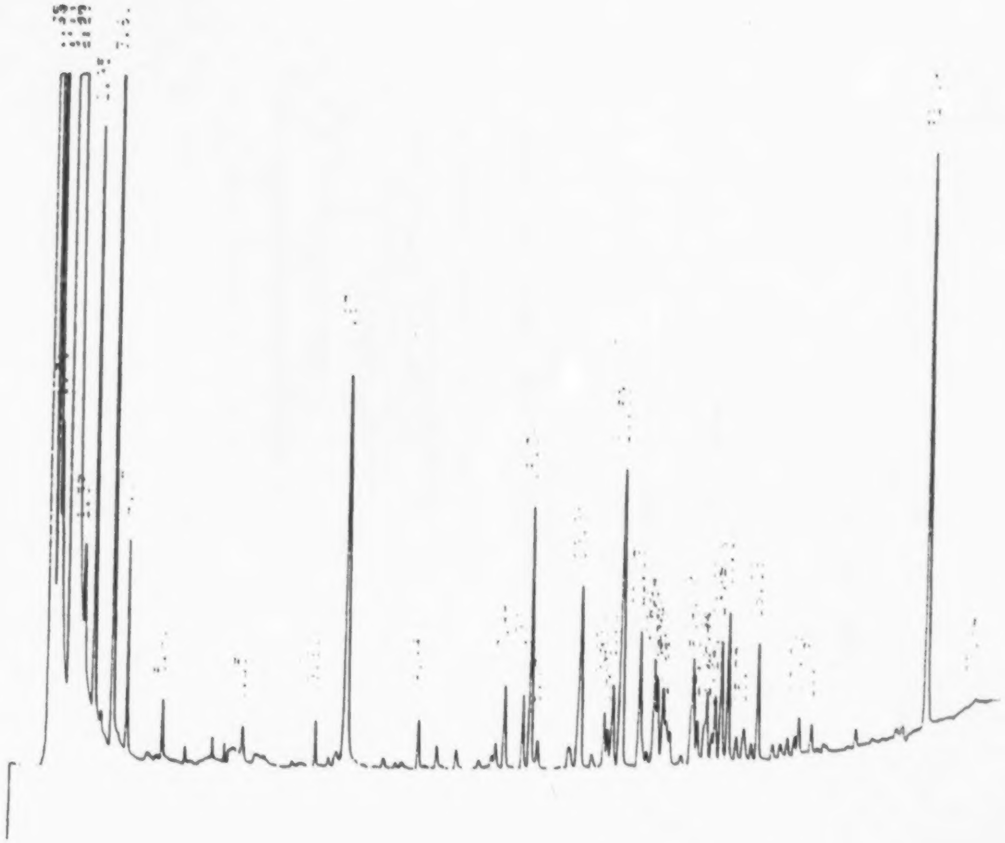

Figure 16. Aroclor 1232 on the DB-608.

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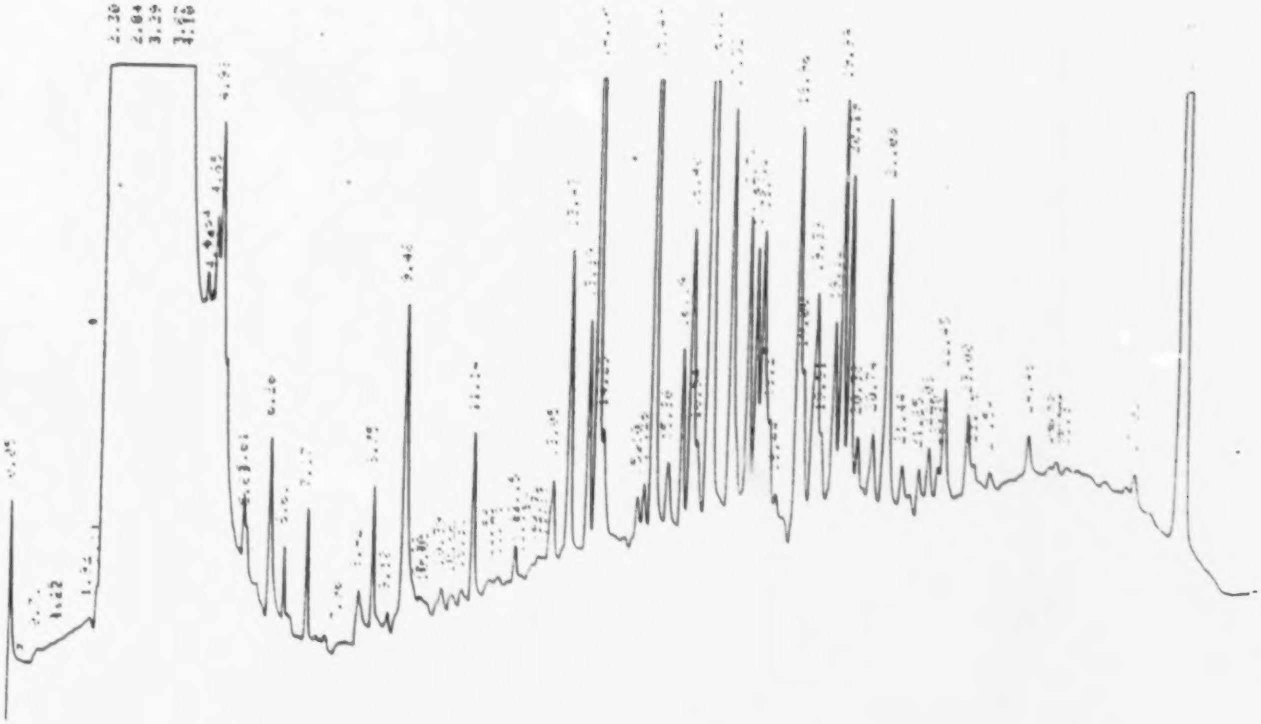

Figure 17. Aroclor 1232 on the SPB-608.

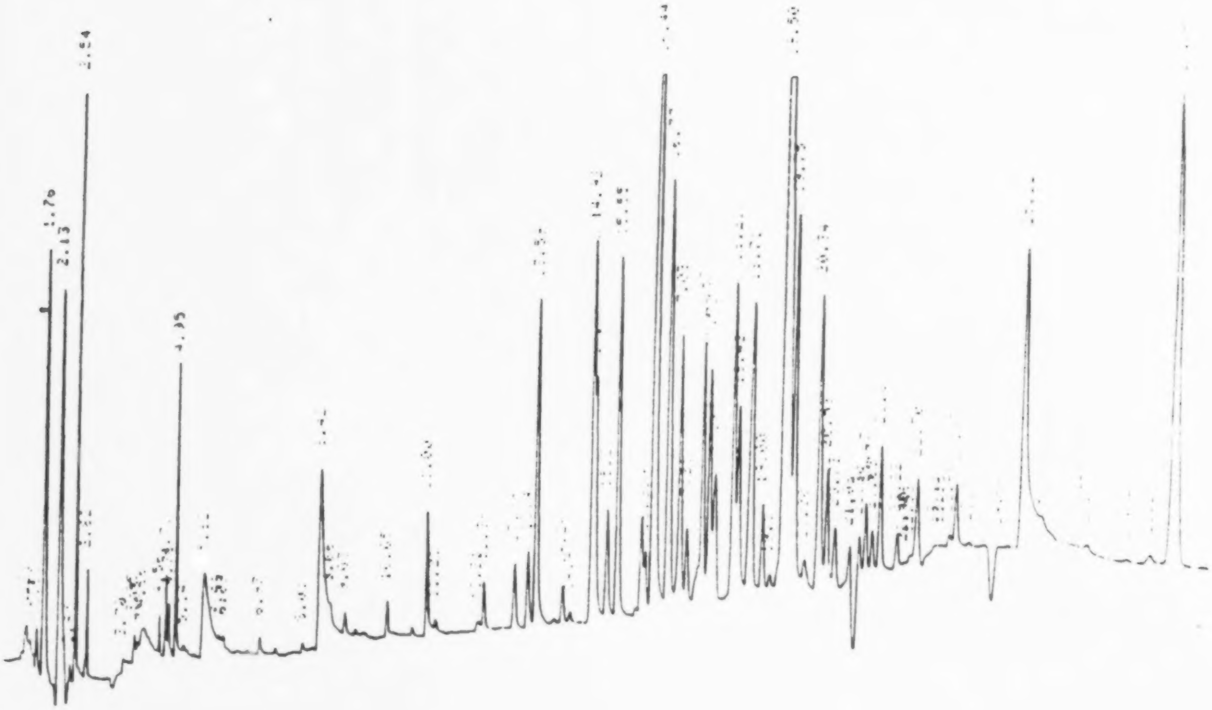

Figure 18. Aroclor 1242 on the DB-5.

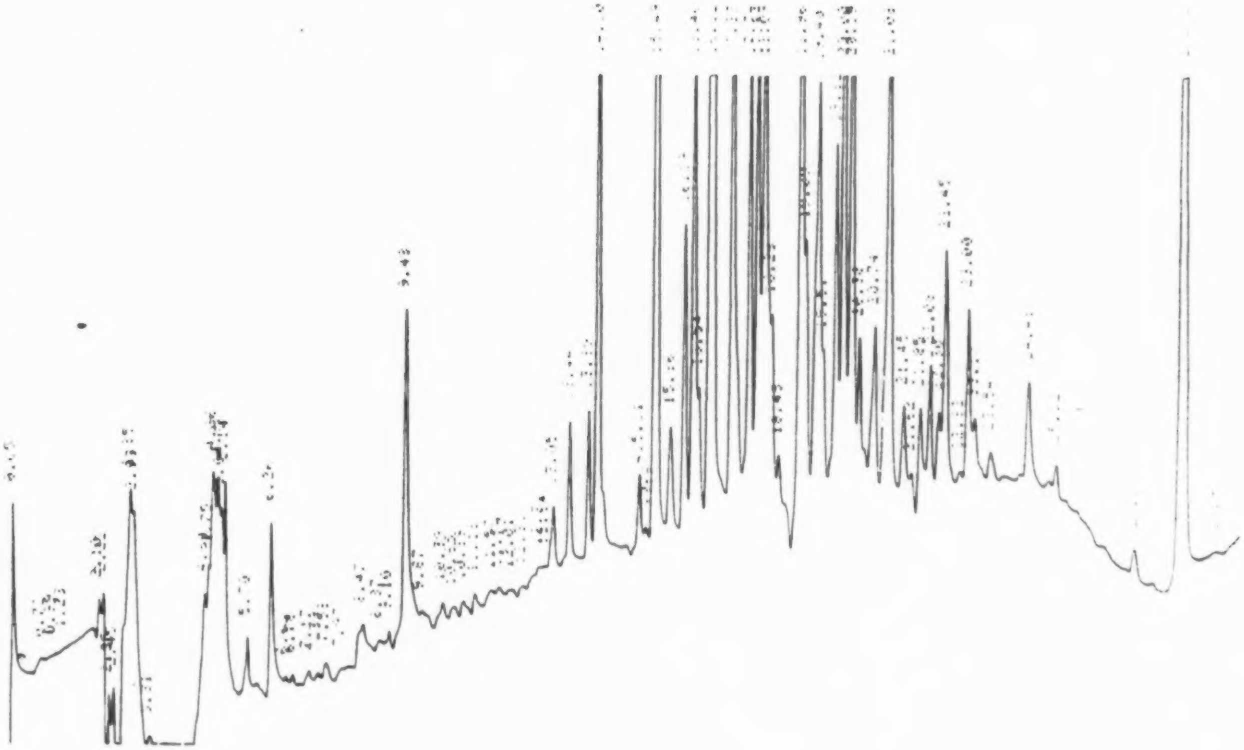

Figure 19. Aroclor 1242 on the SPB-608.

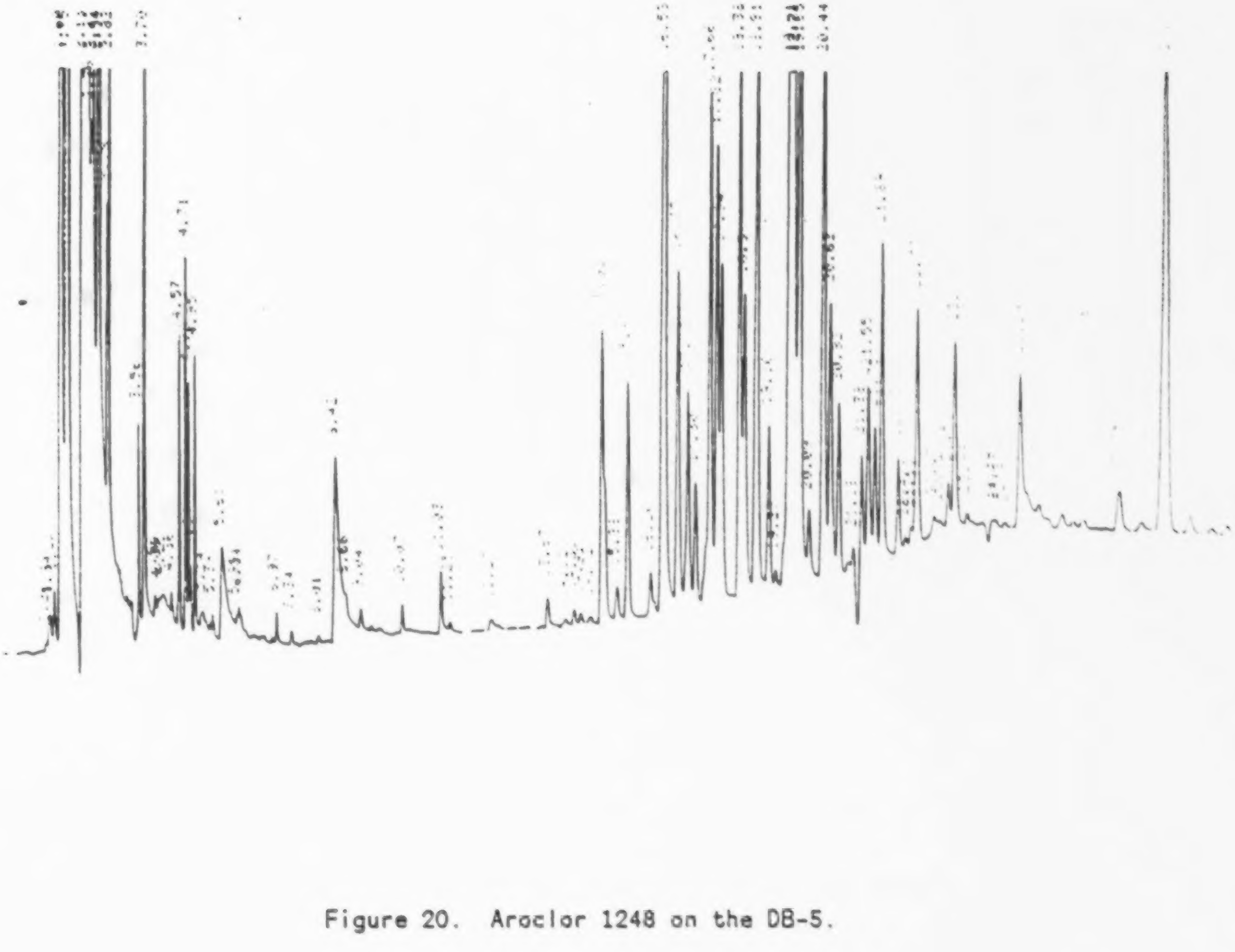

Figure 20. Aroclor 1248 on the DB-5.

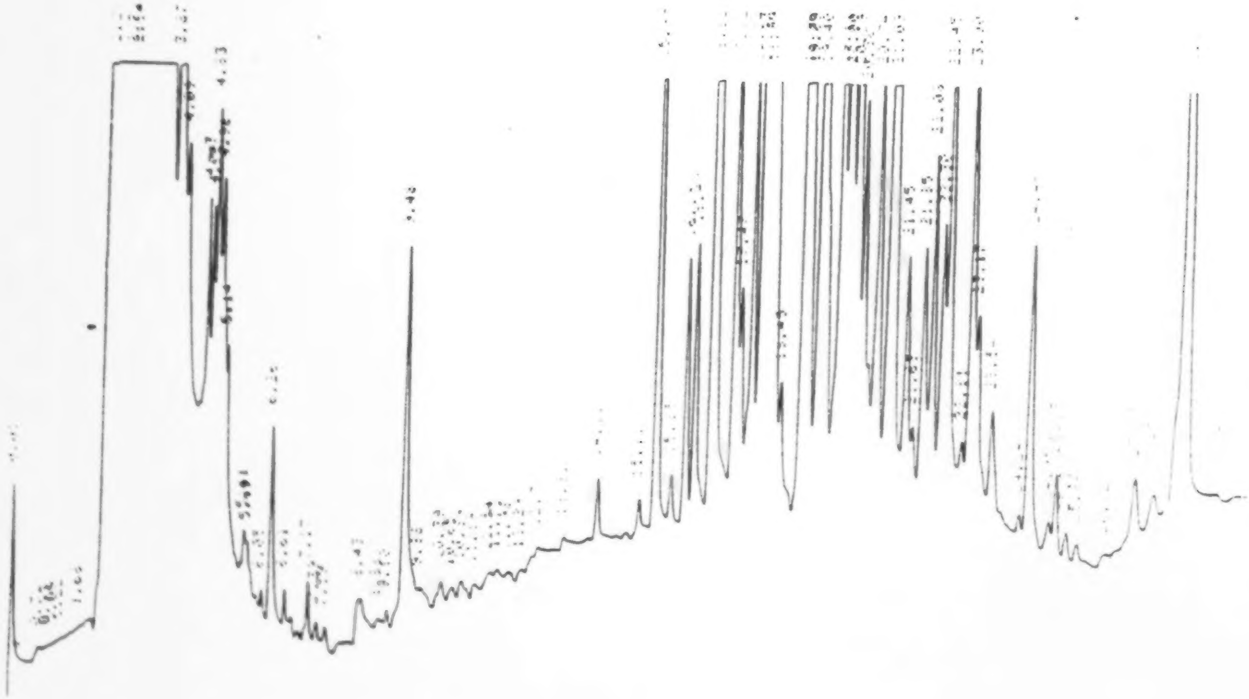

Figure 21. Aroclor 1248 on the SPB-608.

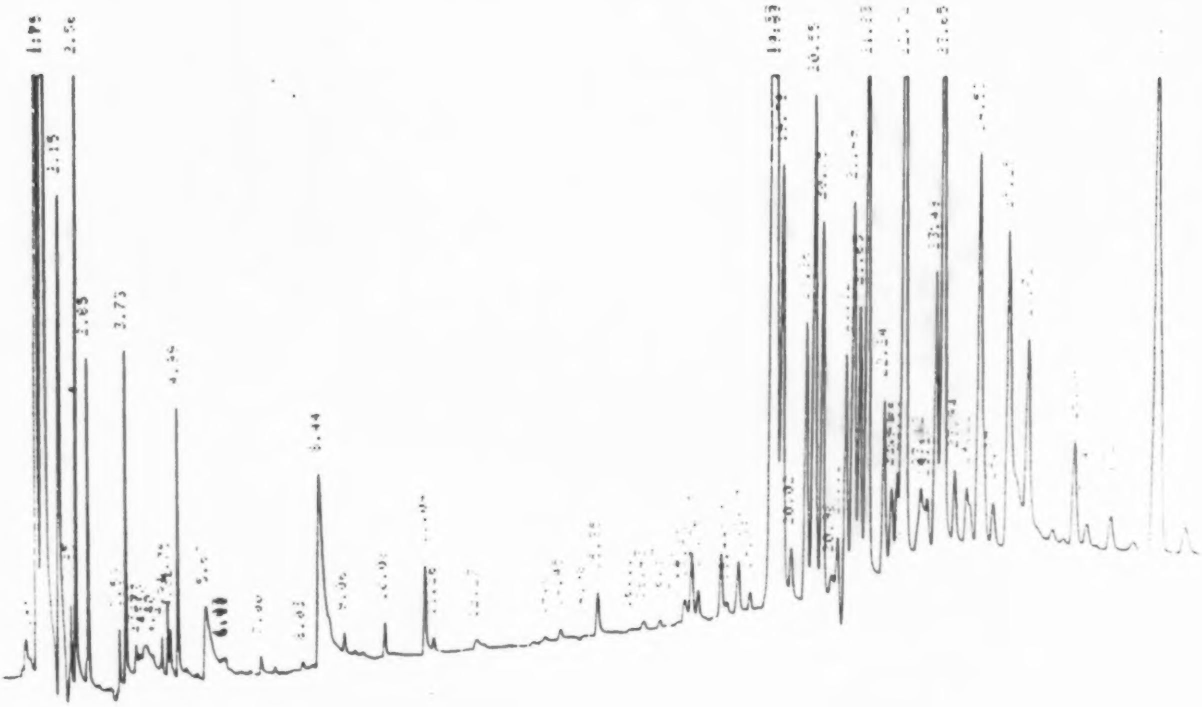

Figure 22. Aroclor 1254 on the DB-5.

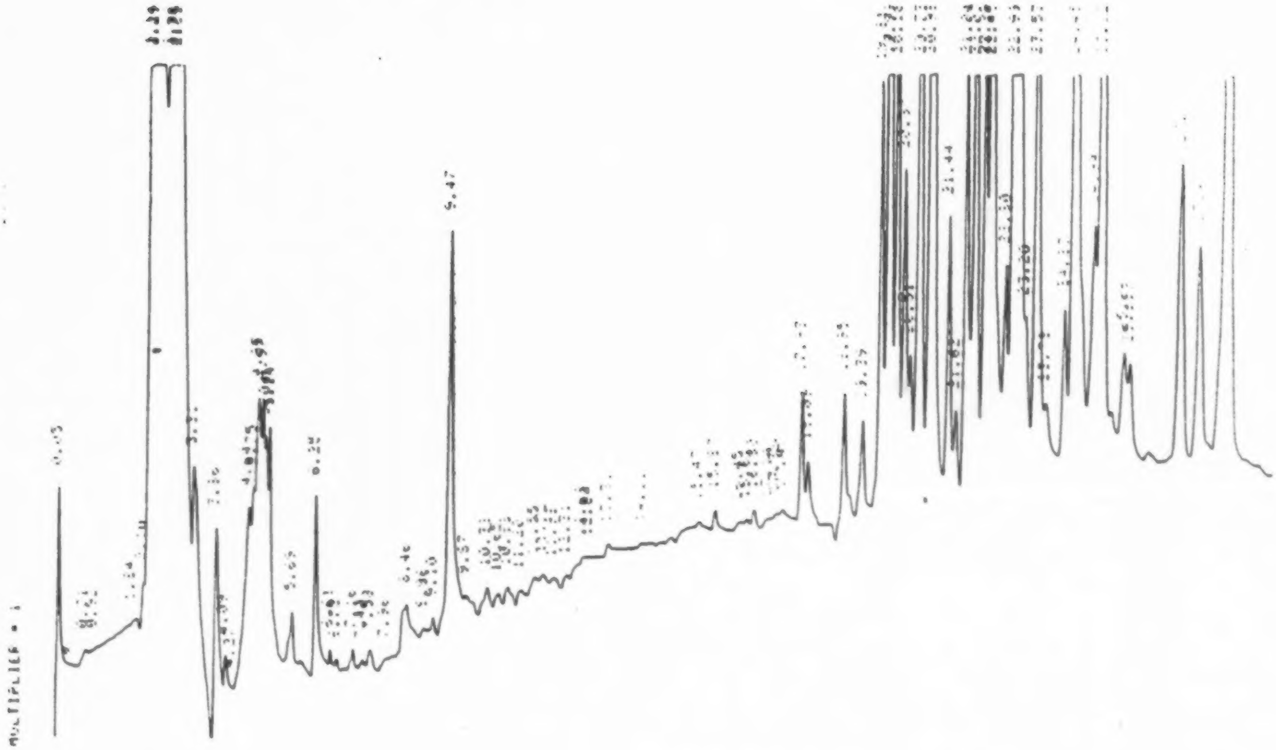

Figure 23. Aroclor 1254 on the SPB-608.

EPA METHOD
NO. 1624C

18 December 1986

Method 1624, Revision C

Volatile Organic Compounds by Isotope Dilution GCMS

1 Scope and application

1.1 This method is designed to determine the volatile toxic organic pollutants associated with the 1976 Consent Decree; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation and Liabilities Act; and other compounds amenable to purge and trap gas chromatography-mass spectrometry (GCMS).

1.2 The chemical compounds listed in tables 1 and 2 may be determined in waters, soils, and municipal sludges by this method. The method is designed to meet the survey requirements of the Environmental Protection Agency.

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The levels in table 3 typify the minimum quantity that can be detected with no interferences present.

1.4 The GCMS portions of this method are for use only by analysts experienced with GCMS or under the close supervision of such qualified persons. Laboratories unfamiliar with analyses of environmental samples by GCMS should run the performance tests in reference 1 before beginning.

2 Summary of method

2.1 The percent solids content of the sample is determined. If the solids content is known or determined to be less than one percent, stable isotopically labeled analogs of the compounds of interest are added to a 5 mL sample and the sample is purged with an inert gas at 20 - 25 °C in a chamber designed for soil or water samples. If the solids content is greater than one percent, five mL of reagent water and the labeled compounds are added to a 5 gram aliquot of sample and the mixture is purged at 40 °C. Compounds that will not purge at 20 - 25 °C or at 40 °C are purged at 75 - 85 °C.

In the purging process, the volatile compounds are transferred from the aqueous phase into the gaseous phase where they are passed into a sorbent column and trapped. After purging is completed, the trap is backflushed and heated rapidly to desorb the compounds into a gas chromatograph (GC). The compounds are separated by the GC and detected by a mass spectrometer (MS) (references 2 and 3). The labeled compounds serve to correct the variability of the analytical technique.

2.2 Identification of a pollutant (qualitative analysis) is performed in one of three ways: (1) For compounds listed in table 1 and other compounds for which authentic standards are available, the GCMS system is calibrated and the mass spectrum and retention time for each standard are stored in a user created library. A compound is identified when its retention time and mass spectrum agree with the library retention time and spectrum. (2) For compounds listed in table 2 and other compounds for which standards are not available, a compound is identified when the retention time and mass spectrum agree with those specified in this method. (3) For chromatographic peaks which are not identified by (1) and (2) above, the background corrected spectrum at the peak maximum is compared with spectra in the EPA/NIH Mass Spectral File (reference 4). Tentative identification is established when the spectrum agrees.

2.3 Quantitative analysis is performed in one of four ways by GCMS using extracted ion current profile (EICP) areas: (1) For compounds listed in table 1 and other compounds for which standards and labeled analogs are available, the GCMS system is calibrated and the compound concentration is determined using an isotope dilution technique. (2) For compounds listed in table 1 and for other compounds for which authentic standards but no labeled compounds are available, the GCMS system is calibrated and the compound concentration is determined using an internal standard technique. (3) For compounds listed in table 2 and other compounds for which standards are not available, compound concentrations are determined using known response factors. (4) For compounds for which neither standards nor known response factors are available, compound concentration is determined using the sum of the EICP areas relative to the sum of the EICP areas of the nearest eluted internal standard.

2.4 Quality is assured through reproducible calibration and testing of the purge and trap and GCMS systems.

3 Contamination and interferences

3.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing upstream of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from interferences under conditions of the analysis by analyzing reagent water blanks initially and with each sample batch (samples analyzed on the same

8 hr shift), as described in section 8.5.

3.2 Samples can be contaminated by diffusion of volatile organic compounds (particularly methylene chloride) through the bottle seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol serves as a check on such contamination.

3.3 Contamination by carry-over can occur when high level and low level samples are analyzed sequentially. To reduce carry-over, the purging device (figure 1 for samples containing less than one percent solids; figure 2 for samples containing one percent solids or greater) is cleaned or replaced with a clean purging device after each sample is analyzed. When an unusually concentrated sample is encountered, it is followed by analysis of a reagent water blank to check for carry-over. Purging devices are cleaned by washing with soap solution, rinsing with tap and distilled water, and drying in an oven at 100-125 °C. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

3.4 Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled.

4 Safety

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 5 - 7.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

5 Apparatus and mater[illegible]

5.1 Sample bottles fo[illegible]rete sampling

5.1.1 Bottle--25 to 40 mL with screw cap (Pierce 13075, or equivalent). Detergent wash, rinse with tap and distilled water, and dry at >105 °C for one hr minimum before use.

5.1.2 Septum--Teflon-faced silicone (Pierce 12722, or equivalent), cleaned as above and baked at 100 - 200 °C for one hour minimum.

5.2 Purge and trap device--consists of purging device, trap, and desorber.

5.2.1 Purging devices for water and soil samples

5.2.1.1 Purging device for water samples--designed to accept 5 mL samples with water column at least 3 cm deep. The volume of the gaseous head space between the water and trap shall be less than 15 mL. The purge gas shall be introduced less than 5 mm from the base of the water column and shall pass through the water as bubbles with a diameter less than 3 mm. The purging device shown in figure 1 meets these criteria.

5.2.1.2 Purging device for solid samples--designed to accept 5 grams of solids plus 5 mL of water. The volume of the gaseous head space between the water and trap shall be less than 25 mL. The purge gas shall be introduced less than 5 mm from the base of the sample and shall pass through the water as bubbles with a diameter less than 3 mm. The purging device shall be capable of operating at ambient temperature (20 - 25 °C) and of being controlled at temperatures of 40 +/- 2 °C and 80 +/- 5 °C while the sample is being purged. The purging device shown in figure 2 meets these criteria.

5.2.2 Trap--25 to 30 cm x 2.5 mm i.d. minimum, containing the following:

5.2.2.1 Methyl silicone packing--one +/- 0.2 cm, 3 percent OV-1 on 60/80 mesh Chromosorb W, or equivalent.

5.2.2.2 Porous polymer--15 +/- 1.0 cm, Tenax GC (2,6-diphenylene oxide polymer), 60/80 mesh, chromatographic grade, or equivalent.

5.2.2.3 Silica gel--8 +/- 1.0 cm, Davison Chemical, 35/60 mesh, grade 15, or equivalent. The trap shown in figure 3 meets these specifications.

5.2.4 Desorber--shall heat the trap to 175 +/- 5 °C in 45 seconds or less. The polymer section of the trap shall not exceed a temperature of 180 °C and the remaining sections shall not exceed 220 °C during desorb, and no portion of the trap shall exceed 225 °C during bakeout. The desorber shown in figure 4 meets these specifications.

5.2.5 The purge and trap device may be a separate unit or coupled to a GC as shown in figures 4 and 5.

5.3 Gas chromatograph--shall be linearly temperature programmable with initial and final holds, shall contain a glass jet separator as the MS interface, and shall produce results which meet the calibration (section 7), quality assurance (section 8), and performance tests (section 11) of this method.

5.3.1 Column--2.8 +/- 0.4 m x 2 +/- 0.5 mm i.d. glass, packed with one percent SP-1000 on Carbopak B, 60/80 mesh, or equivalent.

5.4 Mass spectrometer--70 eV electron impact ionization; shall repetitively scan from 20 to 250 amu every 2-3 seconds, and produce a unit resolution (valleys between m/z 174-176 less than 10 percent of the height of the m/z 175 peak), background corrected mass spectrum from 50 ng 4-bromofluorobenzene (BFB) injected into the GC. The BFB spectrum shall meet the mass-intensity criteria in table 4. All portions of the GC column, transfer lines, and separator which connect the GC column to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

5.5 Data system--shall collect and record MS data, store mass-intensity data in spectral libraries, process GCMS data and generate reports, and shall calculate and record response factors.

5.5.1 Data acquisition--mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

5.5.2 Mass spectral libraries--user created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse search GCMS runs for the compounds of interest (section 7.2).

5.5.3 Data processing--the data system shall be used to search, locate, identify, and quantify the compounds of interest in each GCMS analysis. Software routines shall be employed to compute retention times and EICP areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

5.5.4 Response factors and multipoint calibrations--the data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and generate multi-point calibration curves (section 7). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity. Statistics on initial and on-going performance shall be maintained (sections 8 and 11).

5.6 Syringes--5 mL glass hypodermic, with Luer-lok tips.

5.7 Micro syringes--10, 25, and 100 uL.

5.8 Syringe valves--2-way, with Luer ends (Teflon or Kel-F).

5.9 Syringe--5 mL, gas-tight, with shut-off valve.

5.10 Bottles--15 mL, screw-cap with Teflon liner.

5.11 Balances

5.11.1 Analytical, capable of weighing 0.1 mg.

5.11.2 Top loading, capable of weighing 10 mg.

5.12 Equipment for determining percent moisture

5.12.1 Oven, capable of being temperature controlled at 110 +/- 5 °C.

5.12.2 Dessicator

5.12.3 Beakers--50 - 100 mL

6 Reagents and standards

6.1 Reagent water--water in which the compounds of interest and interfering compounds are not detected by this method (section 11.7). It may be generated by any of the following methods:

6.1.1 Activated carbon--pass tap water through a carbon bed (Calgon Filtrasorb-300, or equivalent).

6.1.2 Water purifier--pass tap water through a purifier (Millipore Super Q, or equivalent).

6.1.3 Boil and purge--heat tap water to 90-100 °C and bubble contaminant free inert gas through it for approx one hour. While still hot, transfer the water to screw-cap bottles and seal with a

Teflon-lined cap.

6.2 Sodium thiosulfate--ACS granular.

6.3 Methanol--pesticide quality or equivalent.

6.4 Standard solutions--purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the standard.

6.5 Preparation of stock solutions--prepare in methanol using liquid or gaseous standards per the steps below. Observe the safety precautions given in section 4.

6.5.1 Place approx 9.8 mL of methanol in a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand unstoppered for approx 10 minutes or until all methanol wetted surfaces have dried. In each case, weigh the flask, immediately add the compound, then immediately reweigh to prevent evaporation losses from affecting the measurement.

6.5.1.1 Liquids--using a 100 uL syringe, permit 2 drops of liquid to fall into the methanol without contacting the neck of the flask. Alternatively, inject a known volume of the compound into the methanol in the flask using a micro-syringe.

6.5.1.2 Gases (chloromethane, bromomethane, chloroethane, vinyl chloride)--fill a valved 5 mL gas-tight syringe with the compound. Lower the needle to approx 5 mm above the methanol meniscus. Slowly introduce the compound above the surface of the meniscus. The gas will dissolve rapidly in the methanol.

6.5.2 Fill the flask to volume, stopper, then mix by inverting several times. Calculate the concentration in mg/mL (ug/uL) from the weight gain (or density if a known volume was injected).

6.5.3 Transfer the stock solution to a Teflon sealed screw-cap bottle. Store, with minimal headspace, in the dark at -10 to -20 °C.

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All other standards are replaced after one month, or sooner if comparison with check standards indicate a change in concentration. Quality control check standards that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

6.6 Labeled compound spiking solution--from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution to contain a concentration such that a 5-10 uL spike into each 5 mL sample, blank, or aqueous standard analyzed will result in a concentration of 20 ug/L of each labeled compound. For the gases and for the water soluble compounds (acrolein, acrylonitrile, acetone, diethyl ether, and MEK), a concentration of 100 ug/L may be used. Include the internal standards (section 7.5) in this solution so that a concentration of 20 ug/L in each sample, blank, or aqueous standard will be produced.

6.7 Secondary standards--using stock solutions, prepare a secondary standard in methanol to contain each pollutant at a concentration of 500 ug/mL. For the gases and water soluble compounds (section 6.6), a concentration of 2.5 mg/mL may be used.

6.7.1 Aqueous calibration standards--using a 25 uL syringe, add 20 uL of the secondary standard (section 6.7) to 50, 100, 200, 500, and 1000 mL of reagent water to produce concentrations of 200, 100, 50, 20, and 10 ug/L respectively. If the higher concentration standard for the gases and water soluble compounds was chosen (section 6.6), these compounds will be at concentrations of 1000, 500, 250, 100 and 50 ug/L in the aqueous calibration standards.

6.7.2 Aqueous performance standard--an aqueous standard containing all pollutants, internal standards, labeled compounds, and BFB is prepared daily, and analyzed each shift to demonstrate performance (section 11). This standard shall contain either 20 or 100 ug/L of the labeled and pollutant gases and water soluble compounds, 10 ug/L BFB, and 20 ug/L of all other pollutants, labeled compounds, and internal standards. It may be the nominal 20 ug/L aqueous calibration standard (section 6.7.1).

6.7.3 A methanolic standard containing all pollutants and internal standards is prepared to demonstrate recovery of these compounds when syringe injection and purge and trap analyses are compared. This standard shall contain either 100 ug/mL or 500 ug/mL of the gases and water soluble compounds, and 100 ug/mL of the remaining pollutants and internal standards (consistent with the amounts in the aqueous performance standard in 6.7.2).

6.7.4 Other standards which may be needed are those for test of BFB performance (section 7.1) and for collection of mass spectra for storage in spectral libraries (section 7.2).

7 Calibration

Calibration of the GCMS system is performed by purging the compounds of interest and their labeled analogs from reagent water at the temperature to be used for analysis of samples.

7.1 Assemble the gas chromatographic apparatus and establish operating conditions given in table 3. By injecting standards into the GC, demonstrate that the analytical system meets the minimum levels in table 3 for the compounds for which calibration is to be performed, and the mass-intensity criteria in table 4 for 50 ng BFB.

7.2 Mass spectral libraries--detection and identification of the compounds of interest are dependent upon the spectra stored in user created libraries.

7.2.1 For the compounds in table 1 and other compounds for which the GCMS is to be calibrated, obtain a mass spectrum of each pollutant and labeled compound and each internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound. Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic m/z's or introduce other distortion.

7.2.3 The authentic reference spectrum is obtained under BFB tuning conditions (section 7.1 and table 4) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. The spectrum may be further edited to remove common interfering masses. If 5 mass spectral peaks cannot be obtained under the scan conditions given in section 5.4, the mass spectrometer may be scanned to an m/z lower than 20 to gain additional spectral information. The spectrum obtained is stored for reverse search and for compound confirmation.

7.2.5 For the compounds in table 2 and other compounds for which the mass spectra, quantitation m/z's, and retention times are known but the instrument is not to be calibrated, add the retention time and reference compound (table 3); the response factor and the quantitation m/z (table 5); and spectrum (Appendix A) to the reverse search library. Edit the spectrum per section 7.2.4, if necessary.

7.3 Assemble the purge and trap device. Pack the trap as shown in figure 3 and condition overnight at 170 - 180 °C by backflushing with an inert gas at a flow rate of 20 - 30 mL/min. Condition traps daily for a minimum of 10 minutes prior to use.

7.3.1 Analyze the aqueous performance standard (section 6.7.2) according to the purge and trap procedure in section 10. Compute the area at the primary m/z (table 5) for each compound. Compare these areas to those obtained by injecting one uL of the methanolic standard (section 6.7.3) to determine compound recovery. The recovery shall be greater than 20 percent for the water soluble compounds (section 6.6), and 60 - 110 percent for all other compounds. This recovery is demonstrated initially for each purge and trap GCMS system. The test is repeated only if the purge and trap or GCMS systems are modified in any way that might result in a change in recovery.

7.3.2 Demonstrate that 100 ng toluene (or toluene-d8) produces an area at m/z 91 (or 99) approx one-tenth that required to exceed the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required.

7.4 Calibration by isotope dilution--the isotope dilution approach is used for the purgeable organic compounds when appropriate labeled compounds are available and when interferences do not preclude the analysis. If labeled compounds are not available, or interferences are present, the internal standard method (section 7.5) is used. A calibration curve encompassing the concentration range of interest is prepared for each compound determined. The relative response (RR) vs concentration (ug/L) is plotted or computed using a linear regression. An example of a calibration curve for toluene using toluene-d8 is given in figure 6. Also shown are the +/- 10 percent error limits (dotted lines). Relative response is determined according to the procedures described below. A minimum of five data points are required for calibration (section 7.4.4).

7.4.1 The relative response (RR) of pollutant to labeled compound is determined from isotope ratio values calculated from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured in the pure pollutant (figure 7A).

R_y = the isotope ratio of pure labeled compound (figure 7B).

R_m = the isotope ratio measured in the analytical mixture of the pollutant and labeled compounds (figure 7C)

The correct way to calculate RR is:

$RR = (R_y - R_m)(R_x + 1)/(R_m - R_x)(R_y + 1)$

If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by the internal standard method (section 7.5).

7.4.2 In most cases, the retention times of the pollutant and labeled compound are the same and isotope ratios (R's) can be calculated from the EICP areas, where:

$R = (\text{area at } m_1/z)/(\text{area at } m_2/z)$

If either of the areas is zero, it is assigned a value of one in the calculations; that is, if: area of m_1/z = 50721, and area of m_2/z = 0, then R = 50721/1 = 50720. The m/z's are always selected such that $R_x > R_y$.

When there is a difference in retention times (RT) between the pollutant and labeled compounds, special precautions are required to determine the isotope ratios. R_x, R_y, and R_m are defined as follows:

R_x = [area m_1/z (at RT_1)]/1

R_y = 1/[area m_2/z (at RT_2)]

R_m = [area m_1/z (at RT_1)]/[area m_2/z (at RT_2)]

7.4.3 An example of the above calculations can be taken from the data plotted in figure 6 for toluene and toluene-d8. For these data, R_x = 168920/1 = 168900, R_y = 1/60960 = 0.00001640, and R_m = 96868/82508 = 1.174. The RR for the above data is then calculated using the equation given in section 7.4.1. For the example, RR = 1.174.

Not all labeled compounds elute before their pollutant analogs.

7.4.4 To calibrate the analytical system by isotope dilution, analyze a 5 mL aliquot of each of the aqueous calibration standards (section 6.7.1) spiked with an appropriate constant amount of the labeled compound spiking solution (section 6.6), using the purge and trap procedure in section 10. Compute the RR at each concentration.

7.4.5 Linearity--if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the 5 point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point calibration range.

7.5 Calibration by internal standard--used when criteria for isotope dilution (section 7.4) cannot be met. The method is applied to pollutants having no labeled analog and to the labeled compounds. The internal standards used for volatiles analyses are bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Concentrations of the labeled compounds and pollutants without labeled analogs are computed relative to the nearest eluted internal standard, as shown in tables 3 and 5.

7.5.1 Response factors--calibration requires the determination of response factors (RF) which are defined by the following equation:

$RF = (A_s \times C_{is})/(A_{is} \times C_s)$, where

A_s is the EICP area at the characteristic m/z for the compound in the daily standard.

A_{is} is the EICP area at the characteristic m/z for the internal standard.

C_{is} is the concentration (ug/L) of the internal standard.

C_s is the concentration of the pollutant in the daily standard.

7.5.2 The response factor is determined at 10, 20, 50, 100, and 200 ug/L for the pollutants (optionally at five times these concentrations for gases and water soluble pollutants--see section 6.7), in a way analogous to that for calibration by isotope dilution (section 7.4.4). The RF is plotted against concentration for each compound in the standard (C_s) to produce a calibration curve.

7.5.3 Linearity--if the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

7.6 Combined calibration--by adding the isotopically labeled compounds and internal standards (section 6.6) to the aqueous calibration standards (section 6.7.1), a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (section 11.5) by purging the aqueous performance standard (section 6.7.2). Recalibration is required only if calibration and on-going performance (section 11.5) criteria cannot be met.

7.7 Elevated purge temperature calibration--samples containing greater than one percent solids are analyzed at a temperature of 40 +/- 2 °C (section 10). For these samples, the analytical system may be calibrated using a purge temperature of 40 +/- 2 ° C in order to more closely approximate the behavior of the compounds of interest in high solids samples.

8 Quality assurance/quality control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program (reference 8). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in section 8.2.

8.1.2 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in section 8.2 to demonstrate method performance.

8.1.3 Analyses of blanks are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis (section 3). The procedures and criteria for analysis of a blank are described in sections 8.5.

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (section 14.2).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through the analysis of the aqueous performance standard (section 6.7.2) that the analysis system is in control. This procedure is described in sections 11.1 and 11.5.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in sections 8.4 and 11.5.2.

8.2 Initial precision and accuracy--to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations for compounds to be calibrated:

8.2.1 Analyze two sets of four 5-mL aliquots (8 aliquots total) of the aqueous performance standard (section 6.7.2) according to the method beginning in section 10.

8.2.2 Using results of the first set of four analyses in section 8.2.1, compute the average recovery (X) in ug/L and the standard deviation of the recovery (s) in ug/L for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

8.2.3 For each compound, compare s and X with the corresponding limits for initial precision and accuracy found in table 6. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 6 present a substantial probability that one or more will fail one of the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.4 Using the results of the second set of four analyses, compute s and X for only those compounds which failed the test of the first set of four analyses (section 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for the compound (s) in question. In this event, correct the problem and repeat the entire test (section 8.2.1).

8.3 The laboratory shall spike all samples with labeled compounds to assess method performance on the sample matrix.

8.3.1 Spike and analyze each sample according to the method beginning in section 10.

8.3.2 Compute the percent recovery (P) of the labeled compounds using the internal standard method (section 7.5).

8.3.3 Compare the percent recovery for each compound with the corresponding labeled compound recovery limit in table 6. If the recovery of any compound falls outside its warning limit, method performance is unacceptable for that compound in that sample. Therefore, the sample matrix is complex and the sample is to be diluted and reanalyzed, per section 14.2.

8.4 As part of the QA program for the laboratory, method accuracy for wastewater samples shall be assessed and records shall be maintained. After the analysis of five wastewater samples for which the labeled compounds pass the tests in section 8.3.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$. For example, if $P = 90\%$ and $s_p = 10\%$, the accuracy interval is expressed as 70 - 110%. Update the accuracy assessment for each compound on a regular basis (e.g. after each 5 - 10 new accuracy measurements).

8.5 Blanks--reagent water blanks are analyzed to demonstrate freedom from carry-over (section 3) and contamination.

8.5.1 The level at which the purge and trap system will carry greater than 5 ug/L of a pollutant of interest (tables 1 and 2) into a succeeding blank shall be determined by analyzing successively larger concentrations of these compounds. When a sample contains this concentration or more, a blank shall be analyzed immediately following this sample to demonstrate no carry-over at the 5 ug/L level.

8.5.2 With each sample lot (samples analyzed on the same 8 hr shift), a blank shall be analyzed immediately after analysis of the aqueous performance standard (section 11.1) to demonstrate freedom from contamination. If any of the compounds of interest (tables 1 and 2) or any potentially interfering compound is found in a blank at greater than 10 ug/L (assuming a response factor of 1 relative to the nearest eluted internal standard for compounds not listed in tables 1 and 2), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

8.6 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (section 7), calibration verification (section 11.5) and for initial (section 8.2) and on-going (section 11.5) precision and accuracy should be identical, so that the most precise results will be obtained. The GCMS instrument in particular will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of volatiles by this method.

8.7 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal method is used.

9 Sample collection, preservation, and handling

9.1 Grab samples are collected in glass containers having a total volume greater than 20 mL. For aqueous samples which pour freely, fill sample bottles so that no air bubbles pass through the sample as the bottle is filled and seal each bottle so that no air bubbles are entrapped. Maintain the hermetic seal on the sample bottle until time of analysis.

9.2 Samples are maintained at 0 - 4 °C from the time of collection until analysis. If an aqueous sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL) to the empty sample bottles just prior to shipment to the sample site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine (reference 9). If preservative has been added, shake the bottle vigorously for one minute immediately after filling.

9.3 For aqueous samples, experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in section 9.1. If residual chlorine is present, add sodium thiosulfate to a separate sample container and fill as in section 9.1.

9.4 All samples shall be analyzed within 14 days of collection.

10 Purge, trap, and GCMS analysis--samples containing less than one percent solids are analyzed directly as aqueous samples (section 10.4). Samples containing greater one percent solids or greater are analyzed as solid samples (section 10.5).

10.1 Determination of percent solids

10.1.1 Weigh 5 - 10 g of sample into a tared beaker.

10.1.2 Dry overnight (12 hours minimum) at 110 +/- 5 °C, and cool in a dessicator.

10.1.3 Determine percent solids as follows:

$$\% \text{ solids} = \frac{\text{weight of sample dry}}{\text{weight of sample wet}} \times 100$$

10.2 Remove standards and samples from cold storage and bring to 20 - 25 °C.

10.3 Adjust the purge gas flow rate to 40 +/- 4 mL/min.

10.4 Samples containing less than one percent solids

10.4.1 Mix the sample by shaking vigorously. Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample bottle and carefully pour the sample into the syringe barrel until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 +/- 0.1 mL. Because this process of taking an aliquot destroys the validity of the sample for future analysis, fill a second syringe at this time to protect against possible loss of data.

10.4.2 Add an appropriate amount of the labeled compound spiking solution (section 6.6) through the valve bore, then close the valve.

10.4.3 Attach the syringe valve assembly to the syringe valve on the purging device. Open both syringe valves and inject the sample into the purging chamber. Purge the sample per section 10.6.

10.5 Weighing of samples containing one percent solids or greater.

10.5.1 Mix the sample thoroughly using a clean spatula.

10.5.2 Weigh 5 +/- 1 grams of sample into a purging vessel (figure 2). Record the weight to three significant figures.

10.5.3 Add 5.0 +/- 0.1 mL of reagent water to the vessel.

10.5.4 Using a metal spatula, break up any lumps of sample to disperse the sample in the water.

10.5.5 Add an appropriate amount of the labeled compound spiking solution (section 6.6) to the sample in the purge vessel. Place a cap on the purging vessel and and shake vigorously to further disperse the sample. Attach the purge vessel to the purging device.

10.6 Purge the sample for 11.0 +/- 0.1 minutes at 20 - 25 °C for samples containing less than one percent solids. Purge samples containing one percent solids or greater at 40 +/- 2 °C. If the compounds in table 2 that do not purge at 20 - 40 °C are to be determined, a purge temperature of 80 +/- 5 °C is used.

10.7 After the 11 minute purge time, attach the trap to the chromatograph and set the purge and trap apparatus to the desorb mode (figure 5). Desorb the trapped compounds into the GC column by heating the trap to 170 -180 °C while backflushing with carrier gas at 20 - 60 mL/min for four minutes. Start MS data acquisition upon start of the desorb cycle, and start the GC column temperature program 3 minutes later. Table 3 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and minimum levels that can be achieved under these conditions. An example of the separations achieved by the column listed is shown in figure 9. Other columns may be used provided the requirements in section 8 are met. If the priority pollutant gases produce GC peaks so broad that the precision and recovery specifications (section 8.2) cannot be met, the column may be cooled to ambient or sub-ambient temperatures to sharpen these peaks.

10.8 After desorbing the sample for four minutes, recondition the trap by purging with purge gas while maintaining the trap temperature at 170 - 180 °C. After approximately seven minutes, turn off the trap heater to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

10.9 While analysis of the desorbed compounds proceeds, remove and clean the purge device. Rinse with tap water, clean with detergent and water, rinse with tap and distilled water, and dry for one hour minimum in an oven at a temperature greater than 150 °C.

11 System performance

11.1 At the beginning of each 8 hr shift during which analyses are performed, system calibration and performance shall be verified for the pollutants and labeled compounds (table 1). For these tests, analysis of the aqueous performance standard (section 6.7.2) shall be used to verify all performance criteria. Adjustment and/or recalibration (per section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may blanks and samples be analyzed.

11.2 BFB spectrum validity--the criteria in table 4 shall be met.

11.3 Retention times--the absolute retention times of the internal standards shall be as follows: bromochloromethane: 653 - 782 seconds; 2-bromo-1-chloropropane: 1270 - 1369 seconds; 1,4-dichlorobutane: 1510 - 1605 seconds. The relative retention times of all pollutants and labeled compounds shall fall within the limits given in table 3.

11.4 GC resolution--the valley height between toluene and toluene-d8 (at m/z 91 and 99 plotted on the same graph) shall be less than 10 percent of the taller of the two peaks.

11.5 Calibration verification and on-going precision and accuracy--compute the concentration of each pollutant (table 1) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant (table 1) which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the calibration data determined in section 7.

11.5.1 For each pollutant and labeled compound, compare the concentration with the corresponding limit for on-going accuracy in table 6. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If any individual value falls outside the range given, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 6 present a substantial probability that one or more will fail the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure may be attributed to probability, proceed as follows:

11.5.1.1 Analyze a second aliquot of the aqueous performance standard (section 6.7.2).

11.5.1.2 Compute the concentration for only those compounds which failed the first test (section 11.5.1). If these compounds now pass, system performance is acceptable for all compounds and analyses of blanks and samples may proceed. If, however, any of the compounds fail again, the measurement system is not performing properly for these compounds. In this event, locate and correct the problem or recalibrate the system (section 7), and repeat the entire test (section 11.1) for all compounds.

11.5.2 Add results which pass the specification in 11.5.1.2 to initial (section 8.2) and previous on-going data. Update QC charts to form a graphic representation of laboratory performance (figure 8).

Develop a statement of accuracy for each pollutant and labeled compound by calculating the average percent recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy as a recovery interval from R - $2s_r$ to R + $2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85 - 105 percent.

12 Qualitative determination--identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the mass spectral libraries. For compounds for which the relative retention times and mass spectra are known, identification is confirmed per sections 12.1 and 12.2. For unidentified GC peaks, the spectrum is compared to spectra in the EPA/NIH mass spectral file per section 12.3.

12.1 Labeled compounds and pollutants having no labeled analog (tables 1 and 2):

12.1.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.1.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

12.1.3 For the compounds for which the system has been calibrated (table 1), the relative retention time shall be within the windows specified in table 3.

12.1.4 For the compounds for which the system has not been calibrated but the relative retention times and mass spectra are known (table 2), the retention time relative to the internal standard specified in table 3 shall be within +/- 20 scans or +/- 60 seconds, whichever is greater, based on the nominal relative retention time specified in table 3.

12.2 Pollutants having a labeled analog (table 1):

12.2.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.2.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two for all masses stored in the spectral library.

13.2.3 The relative retention time between the pollutant and its labeled analog shall be within the windows specified in table 3.

12.3 Unidentified GC peaks

12.3.1 The signals for m/z's specific to a GC peak shall all maximize within the same two consecutive scans.

12.3.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two with the masses stored in the EPA/NIH Mass Spectral File.

12.4 M/z's present in the experimental mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the experimental mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (section 1.4) is to determine the presence or absence of the compound.

13 Quantitative determination

13.1 Isotope dilution--by adding a known amount of a labeled compound to every sample prior to purging, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon purging, desorption, and gas chromatography. Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the toluene example given in figure 7 (section 7.4.3), RR would be equal to 1.174. For this RR value, the toluene calibration curve given in figure 6 indicates a concentration of 31.8 ug/L.

13.2 Internal standard--calculate the concentration using the response factor determined from calibration data (section 7.5) for the compounds which were calibrated (table 1), or from table 5 for compounds which were not calibrated (table 2), using the following equation:

$$\text{Concentration} = (A_s \times C_{is})/(A_{is} \times RF)$$

where the terms are as defined in section 7.5.1.

13.3 The concentration of the pollutant in the solid phase of the sample is computed using the concentration of the pollutant detected in the aqueous solution, as follows:

$$\text{Concentration in solid (ug/kg)} = \frac{0.005\ \text{L} \times \text{aqueous conc (ug/L)}}{0.01 \times \%\ \text{solids (g)}}$$

where "% solids" is from section 10.1.3.

13.4 If the EICP area at the quantitation m/z exceeds the calibration range of the system, the sample is diluted with reagent water by successive factors of 10 and the dilutions are analyzed until the area is within the calibration range.

13.5 For GC peaks which are to be identified (per section 12.3), the sample is diluted by successive factors of 10 when any peak in the uncorrected mass spectrum at the GC peak maximum is saturated.

13.6 Report results for all pollutants, labeled compounds, and tentatively identified compounds found in all standards, blanks, and samples, in ug/L for samples containing less than one percent solids and in ug/kg for samples in which the undilute sample contains one percent solids or greater, to three significant figures. Results for samples which have been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 13.4) or at which no m/z in the spectrum is saturated (section 13.5). For compounds having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 13.4) and the labeled compound recovery is within the normal range for the method (section 14.2).

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14 Analysis of complex samples

14.1 Some samples may contain high levels (>1000 ug/kg) of the compounds of interest and of interfering compounds. Some samples will foam excessively when purged; others will overload the trap/or GC column.

14.2 Dilute 0.5 mL of samples containing less than one percent solids or 0.5 gram of samples containing one percent solids or greater with 4.5 mL of reagent water and analyze this diluted sample when the recovery of any labeled compound is outside the range given in table 6. If the recovery remains outside of the range for this diluted sample, the aqueous performance standard shall be analyzed (section 11) and calibration verified (section 11.5). If the recovery for the labeled compound in the aqueous performance standard is outside the range given in table 6, the analytical system is out of control. In this case, the instrument shall be repaired, the performance specifications in section 11 shall be met, and the analysis of the undiluted sample shall be repeated. If the recovery for the aqueous performance standard is within the range given in table 6, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

14.3 Reverse search computer programs can misinterpret the spectrum of chromatographically unresolved pollutant and labeled compound pairs with overlapping spectra when a high level of the pollutant is present. Examine each chromatogram for peaks greater than the height of the internal standard peaks. These peaks can obscure the compounds of interest.

15 Method performance

15.1 The specifications for this method were taken from the interlaboratory validation of EPA Method 624 (reference 10). Method 1624 has been shown to yield slightly better performance on treated effluents than method 624. Results of initial tests of this method at a purge temperature of 80 °C can be found in reference 11 and results of initial tests of this method on municipal sludge can be found in reference 12.

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Table 1

Volatile Organic Compounds Determined by Calibrated GCMS using Isotope Dilution and Internal Standard Techniques

	Pollutant				Labeled Compound		
Compound	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
acetone	81552	67-64-1	516 V		d6	666-52-4	616 V
acrolein	34210	107-02-8	002 V	001 V	d4	33984-05-3	202 V
acrylonitrile	34215	107-13-1	003 V	002 V	d3	53807-26-4	203 V
benzene	34030	71-43-2	004 V	003 V	d6	1076-43-3	204 V
bromodichloromethane	32101	75-27-4	048 V	012 V	13C	93952-10-4	248 V
bromoform	32104	75-25-2	047 V	005 V	13C	72802-81-4	247 V
bromomethane	34413	74-83-9	046 V	020 V	d3	1111-88-2	246 V
carbon tetrachloride	32102	56-23-5	006 V	006 V	13C	32488-50-9	206 V
chlorobenzene	34301	108-90-7	007 V	007 V	d5	3114-55-4	207 V
chloroethane	34311	75-00-3	016 V	009 V	d5	19199-91-8	216 V
2-chloroethylvinyl ether	34576	110-75-8	019 V	010 V			
chloroform	32106	67-66-3	023 V	011 V	13C	31717-44-9	223 V
chloromethane	34418	74-87-3	045 V	021 V	d3	1111-89-3	245 V
dibromochloromethane	32105	124-48-1	051 V	008 V	13C	93951-99-6	251 V
1,1-dichloroethane	34496	75-34-3	013 V	014 V	d3	56912-77-7	213 V
1,2-dichloroethane	32103	107-06-2	010 V	015 V	d4	17070-07-0	210 V
1,1-dichloroethene	34501	75-35-4	029 V	016 V	d2	22280-73-5	229 V
trans-1,2-dichlorethene	34546	156-60-5	030 V	026 V	d3	42366-47-2	230 V
1,2-dichloropropane	34541	78-87-5	032 V	017 V	d6	93952-08-0	232 V
trans-1,3-dichloropropene	34699	10061-02-6	033 V		d4	93951-86-1	233 V
diethyl ether	81576	60-29-7	515 V		d10	2679-89-2	615 V
p-dioxane	81582	123-91-1	527 V		d8	17647-74-4	627 V
ethylbenzene	34371	100-41-4	038 V	019 V	d10	25837-05-2	238 V
methylene chloride	34423	75-09-2	044 V	022 V	d2	1665-00-5	244 V
methyl ethyl ketone	81595	78-93-3	514 V		d5	53389-26-7	614 V
1,1,2,2-tetrachloroethane	34516	79-34-5	015 V	023 V	d2	33685-54-0	215 V
tetrachlorethene	34475	127-18-4	085 V	024 V	13C2	32488-49-6	285 V
toluene	34010	108-88-3	086 V	025 V	d8	2037-26-5	286 V
1,1,1-trichloroethane	34506	71-55-6	011 V	027 V	d3	2747-58-2	211 V
1,1,2-trichloroethane	34511	79-00-5	014 V	028 V	13C2	93952-09-1	214 V
trichloroethene	39180	79-01-6	087 V	029 V	13C2	93952-00-2	287 V
vinyl chloride	39175	75-01-4	088 V	031 V	d3	6745-35-3	288 V

Table 2

Volatile Organic Compounds to be Determined by Reverse Search and Quantitation using Known Retention Times, Response Factors, Reference Compounds, and Mass Spectra

EGD No.	Compound	CAS Registry
532	allyl alcohol*	107-18-6
533	carbon disulfide	75-15-0
534	2-chloro-1,3-butadiene (chloroprene)	126-99-8
535	chloroacetonitrile*	107-14-2
536	3-chloropropene	107-05-1
537	crotonaldehyde*	123-73-9
538	1,2-dibromoethane (EDB)	106-93-4
539	dibromomethane	74-95-3
540	trans-1,4-dichloro-2-butene	110-47-6
541	1,3-dichloropropane	142-28-9
542	cis-1,3-dichloropropene	10061-01-5
543	ethyl cyanide*	107-12-0
544	ethyl methacrylate	97-63-2
545	2-hexanone	591-78-6
546	iodomethane	74-88-4
547	isobutyl alcohol*	78-83-1
548	methacrylonitrile	126-98-7
549	methyl methacrylate	78-83-1
550	4-methyl-2-pentanone	108-10-1
551	1,1,1,2-tetrachloroethane	630-20-6
552	trichlorofluoromethane	75-69-4
553	1,2,3-trichloropropane	96-18-4
554	vinyl acetate	108-05-4

*determined at a purge temperature of 75 - 85 °C

Table 3

Gas Chromatography of Purgeable Organic Compounds

EGD No. (1)	Compound	Retention time Mean (sec)	Retention time EGD Ref	Retention time Relative (2)	Minimum level (3) (ug/L)	Method Detection Limit (4) Low solids (ug/kg)	Method Detection Limit (4) High solids (ug/kg)
245	chloromethane-d3	147	181	0.141 - 0.270	50		
345	chloromethane	148	245	0.922 - 1.210	50	207*	13
246	bromomethane-d3	243	181	0.233 - 0.423	50		
346	bromomethane	246	246	0.898 - 1.195	50	148*	11
288	vinyl chloride-d3	301	181	0.286 - 0.501	50		
388	vinyl chloride	304	288	0.946 - 1.023	10	190*	11
216	chloroethane-d5	378	181	0.373 - 0.620	50		
316	chloroethane	386	216	0.999 - 1.060	50	789*	24
244	methylene chloride-d2	512	181	0.582 - 0.813	10		
344	methylene chloride	517	244	0.999 - 1.017	10	566*	280*
546	iodomethane	498	181	0.68			
616	acetone-d6	554	181	0.628 - 0.889	50		
716	acetone	565	616	0.984 - 1.019	50	3561*	322*
202	acrolein-d4	564	181	0.641 - 0.903(5)	50		
302	acrolein	566	202	0.984 - 1.018(5)	50	377*	18
203	acrylonitrile-d3	606	181	0.735 - 0.926	50		
303	acrylonitrile	612	203	0.985 - 1.030	50	360*	9
533	carbon disulfide	631	181	0.86			
552	trichlorofluoromethane	663	181	0.91			
543	ethyl cyanide	672	181	0.92			
229	1,1-dichloroethene-d2	696	181	0.903 - 0.976	10		
329	1,1-dichloroethene	696	229	0.999 - 1.011	10	31	5
536	3-chloropropene	696	181	0.95			
532	allyl alcohol	703	181	0.96			
181	bromochloromethane (I.S.)	730	181	1.000 - 1.000	10		
213	1,1-dichloroethane-d3	778	181	1.031 - 1.119	10		
313	1,1-dichloroethane	786	213	0.999 - 1.014	10	16	1
615	diethyl ether-d10	804	181	1.067 - 1.254	50		
715	diethyl ether	820	615	1.010 - 1.048	50	63	12
230	trans-1,2-dichloroethene-d2	821	181	1.056 - 1.228	10		
330	trans-1,2-dichloroethene	821	230	0.996 - 1.011	10	41	3
614	methyl ethyl ketone-d3	840	181	0.646 - 1.202	50		
714	methyl ethyl ketone	848	614	0.992 - 1.035	50	241*	80*
223	chloroform-13C1	861	181	1.092 - 1.322	10		
323	chloroform	861	223	0.961 - 1.009	10	21	2
535	chloroacetonitrile	884	181	1.21			
210	1,2-dichloroethane-d4	901	181	1.187 - 1.416	10		
310	1,2-dichloroethane	910	210	0.973 - 1.032	10	23	3
539	dibromomethane	910	181	1.25			
548	methacrylonitrile	921	181	1.26			
547	isobutyl alcohol	962	181	1.32			
211	1,1,1-trichloroethane-13C2	989	181	1.293 - 1.598	10		
311	1,1,1-trichloroethane	999	211	0.989 - 1.044	10	16	4
627	p-dioxane-d8	982	181	1.262 - 1.448(5)	10		
727	p-dioxane	1001	627	1.008 - 1.040(5)	10	--	140*
206	carbon tetrachloride-13C1	1018	182	0.754 - 0.805	10		
306	carbon tetrachloride	1018	206	0.938 - 1.005	10	87	9
554	vinyl acetate	1031	182	0.79			
248	bromodichloromethane-13C1	1045	182	0.766 - 0.825	10		

348	bromodichloromethane	1045	248	0.978 - 1.013	10	28	3
534	2-chloro-1,3-butadiene	1084	182	0.83			
537	crotonaldehyde	1098	182	0.84			
232	1,2-dichloropropane-d6	1123	182	0.830 - 0.880	10		
332	1,2-dichloropropane	1134	232	0.984 - 1.018	10	29	5
542	cis-1,3-dichloropropene	1138	182	0.87			
287	trichloroethene-13C2	1172	182	0.897 - 0.917	10		
387	trichloroethene	1187	287	0.991 - 1.037	10	41	2
541	1,3-dichloropropane	1196	182	0.92			
204	benzene-d6	1200	182	0.888 - 0.952	10		
304	benzene	1212	204	1.002 - 1.026	10	23	8
251	chlorodibromomethane-13C1	1222	182	0.915 - 0.949	10		
351	chlorodibromomethane	1222	251	0.989 - 1.030	10	15	2
214	1,1,2-trichloroethane-13C2	1224	182	0.922 - 0.953	10		
314	1,1,2-trichloroethane	1224	214	0.975 - 1.027	10	26	1
233	trans-1,3-dichloropropene-d4	1226	182	0.922 - 0.959	10		
333	trans-1,3-dichloropropene	1226	233	0.993 - 1.016	10	(6)*	(6)*
019	2-chloroethylvinyl ether	1278	182	0.983 - 1.026	10	122	21
538	1,2-dibromoethane	1279	182	0.98			
182	2-bromo-1-chloropropene (I.S.)	1306	182	1.000 - 1.000	10		
549	methyl methacrylate	1379	182	1.06			
247	bromoform-13C1	1386	182	1.048 - 1.087	10		
347	bromoform	1386	247	0.992 - 1.003	10	91	7
551	1,1,1,2-tetrachloroethane	1408	182	1.08			
550	4-methyl-2-pentanone	1435	183	0.92			
553	1,2,3-trichloropropane	1520	183	0.98			
215	1,1,2,2-tetrachloroethane-d2	1525	183	0.969 - 0.996	10		
315	1,1,2,2-tetrachloroethane	1525	215	0.890 - 1.016	10	20	6
545	2-hexanone	1525	183	0.98			
285	tetrachloroethene-13C2	1528	183	0.966 - 0.996	10		
385	tetrachloroethene	1528	285	0.997 - 1.003	10	106	10
540	trans-1,4-dichloro-2-butene	1551	183	1.00			
183	1,4-dichlorobutane (int std)	1555	183	1.000 - 1.000	10		
544	ethyl methacrylate	1594	183	1.03			
286	toluene-d8	1603	183	1.016 - 1.054	10		
386	toluene	1619	286	1.001 - 1.019	10	27	4
207	chlorobenzene-d5	1679	183	1.066 - 1.135	10		
307	chlorobenzene	1679	207	0.914 - 1.019	10	21	58*
238	ethylbenzene-d10	1802	183	1.144 - 1.293	10		
338	ethylbenzene	1820	238	0.981 - 1.018	10	28	4
185	bromofluorobenzene	1985	183	1.255 - 1.290	10		

(1) Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.
(2) Based on data from a single wastewater laboratory.
(3) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points when calibrated using reagent water. The concentration in the aqueous or solid phase is determined using the equations in section 13.
(4) Method detection limits determined in digested sludge (low solids) and in filter cake or compost (high solids).
(5) Specification derived from related compound.
(6) An unknown interference in the particular sludge studied precluded measurement of the Method Detection Limit (MDL) for this compound.
*Background levels of these compounds were present in the sludge resulting

in higher than expected MDL's. The MDL for these compounds is expected to be approximately 20 ug/kg (100 - 200 for the gases and water soluble compounds) for the low solids method and 5 - 10 ug/kg (25 - 50 for the gases and water soluble compounds) for the high solids method, with no interferences present.

Column: 2.4 m (8 ft) x 2 mm i.d. glass, packed with one percent SP-1000 coated on 60/80 Carbopak B.
Carrier gas: helium at 40 mL/min.
Temperature program: 3 min at 45 °C, 8 °C per min to 240 °C, hold at 240 °C for 15 minutes.
Note: The retention time specifications in this table were developed from data collected from four wastewater laboratories.

Table 4

BFB Mass-intensity Specifications

M/z	Intensity required
50	15 to 40 percent of m/z 95
75	30 to 60 percent of m/z 95
95	base peak, 100 percent
96	5 to 9 percent of m/z 95
173	less than 2 percent of m/z 174
174	greater than 50 percent of m/z 95
175	5 to 9 percent of m/z
176	95 to 100 percent of m/z 174
177	5 to 9 percent of m/z 176

Table 5

Volatile Organic Compound Characteristic M/z's

Compound	Labeled analog	Primary m/z's	Reference compound (1)	Response factor at purge temp. of	
				20 ºC	80 ºC
acetone	d6	58/64			
acrolein	d4	56/60			
acrylonitrile	d3	53/56			
allyl alcohol		57	181	(2)	0.20
benzene	d6	78/84			
2-bromo-1-chloropropane (3)		77			
bromochloromethane (3)		128			
bromodichloromethane	^{13}C	83/86			
bromoform	^{13}C	173/176			
bromomethane	d3	96/99			
carbon disulfide		76	181	1.93	2.02
carbon tetrachloride	^{13}C	47/48			
2-chloro-1,3-butadiene		53	182	0.29	0.50
chloroacetonitrile		75	181	(2)	1.12
chlorobenzene	d5	112/117			
chloroethane	d5	64/71			
2-chloroethylvinyl ether	d7	106/113			
chloroform	^{13}C	85/86			
chloromethane	d3	50/52			
3-chloropropene		76	181	0.43	0.63
crotonaldehyde		70	182	(2)	0.090
dibromochloromethane	^{13}C	129/130			
1,2-dibromoethane		107	182	0.86	0.68
dibromomethane		93	181	1.35	1.91
1,4-dichlorobutane (3)		55			
trans-1,4-dichloro-2-butene		75	183	0.093	0.14
1,1-dichloroethane	d3	63/66			
1,2-dichloroethane	d4	62/67			
1,1-dichloroethene	d2	61/65			
trans-1,2-dichlorethene	d2	61/65			
1,2-dichloropropane	d6	63/67			
1,3-dichloropropane		76	182	0.89	0.88
cis-1,3-dichloropropene		75	182	0.29	0.41
trans-1,3-dichloropropene	d4	75/79			
diethyl ether	d10	74/84			
p-dioxane	d8	88/96			
ethyl cyanide		54	181	(2)	1.26
ethyl methacrylate		69	183	0.69	0.52
ethylbenzene	d10	106/116			
2-hexanone		58	183	0.076	0.33
iodomethane		142	181	4.55	2.55
isobutyl alcohol		74	181	(2)	0.22
methylene chloride	d2	84/88			
methyl ethyl ketone	d3	72/75			
methyl methacrylate		69	182	0.23	0.79
4-methyl-2-pentanone		58	183	0.15	0.29
methacrylonitrile		67	181	0.25	0.79
1,1,1,2-tetrachloroethane		131	182	0.20	0.25
1,1,2,2-tetrachloroethane	d2	83/84			
tetrachlorethene	$^{13}C2$	166/172			

toluene	d8	92/99			
1,1,1-trichloroethane	d3	97/102			
1,1,2-trichloroethane	^{13}C2	83/84			
trichloroethene	^{13}C2	95/136			
trichlorofluoromethane		101	181	2.31	2.19
1,2,3-trichloropropane		75	183	0.89	0.72
vinyl acetate		86	182	0.054	0.19
vinyl chloride	d3	62/65			

(1) 181 = bromochloromethane
182 = 2-bromo-1-chloropropane
183 = 1,4-dichlorobutane
(2) not detected at a purge temperature of 25 °C
(3) internal standard

Table 6

Acceptance Criteria for Performance Tests

	Acceptance criteria at 20 ug/L or as noted			
	Initial precision and accuracy Section 8.2.3		labeled compound recovery Sec 8.3 and 14.2	On-going accuracy Sec 11.5
Compound	s (ug/L)	X (ug/L)	P (%)	R (ug/L)
acetone*	51.	77 - 153	35 - 165	55 - 145
acrolein*	72.	32 - 168	37 - 163	7 - 190
acrylonitrile*	16.	70 - 132	ns - 204	58 - 144
benzene	9.0	13 - 28	ns - 196	4 - 33
bromodichloromethane	8.2	7 - 32	ns - 99	4 - 34
bromoform	7.0	7 - 35	ns - 214	6 - 36
bromomethane	25.	d - 54	ns - 414	d - 61
carbon tetrachloride	6.9	16 - 25	42 - 165	12 - 30
chlorobenzene	8.2	14 - 30	ns - 205	4 - 35
chloroethane	15.	d - 47	ns - 308	d - 51
2-chloroethylvinyl ether	36.	d - 70	ns - 554	d - 79
chloroform	7.9	12 - 26	18 - 172	8 - 30
chloromethane	26.	d - 56	ns - 410	d - 64
dibromochloromethane	7.9	11 - 29	16 - 185	8 - 32
1,1-dichloroethane	6.7	11 - 31	23 - 191	9 - 33
1,2-dichloroethane	7.7	12 - 30	12 - 192	8 - 33
1,1-dichloroethene	12.	d - 50	ns - 315	d - 52
trans-1,2-dichlorethene	7.4	11 - 32	15 - 195	8 - 34
1,2-dichloropropane	19.	d - 47	ns - 343	d - 51
cis-1,3-dichloropropene	22.	d - 51	ns - 381	d - 56
trans-1,3-dichloropropene	15.	d - 40	ns - 284	d - 44
diethyl ether*	44.	75 - 146	44 - 156	55 - 145
p-dioxane	7.2	13 - 27	ns - 239	11 - 29
ethylbenzene	9.6	16 - 29	ns - 203	5 - 35
methylene chloride	9.7	d - 50	ns - 316	d - 50
methyl ethyl ketone*	57.	66 - 159	36 - 164	42 - 158
1,1,2,2-tetrachloroethane	9.6	11 - 30	5 - 199	7 - 34
tetrachlorethene	6.6	15 - 29	31 - 181	11 - 32
toluene	6.3	15 - 29	4 - 193	6 - 33
1,1,1-trichloroethane	5.9	11 - 33	12 - 200	8 - 35
1,1,2-trichloroethane	7.1	12 - 30	21 - 184	9 - 32
trichloroethene	8.9	17 - 30	35 - 196	12 - 34
vinyl chloride	228	d - 59	ns - 452	d - 65

* Acceptance criteria at 100 ug/L

d = detected; result must be greater than zero.

ns = no specification; limit would be below detection limit.

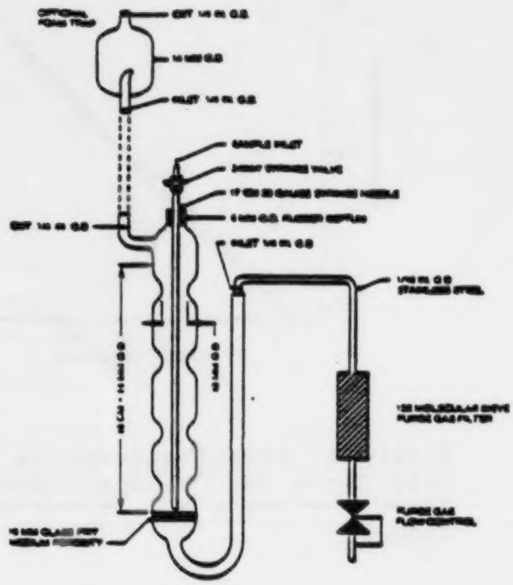

OPTIONAL FOAM TRAP
EXIT 1/4 IN. O.D.
14 MM O.D.
INLET 1/4 IN. O.D.
SAMPLE INLET
2-WAY SYRINGE VALVE
17 CM 20 GAUGE SYRINGE NEEDLE
6 MM O.D. RUBBER SEPTUM
EXIT 1/4 IN. O.D.
INLET 1/4 IN. O.D.
1/16 IN. O.D. STAINLESS STEEL
13X MOLECULAR SIEVE PURGE GAS FILTER
PURGE GAS FLOW CONTROL
10 MM GLASS FRIT MEDIUM POROSITY

Figure 1 Purging Device for Waters

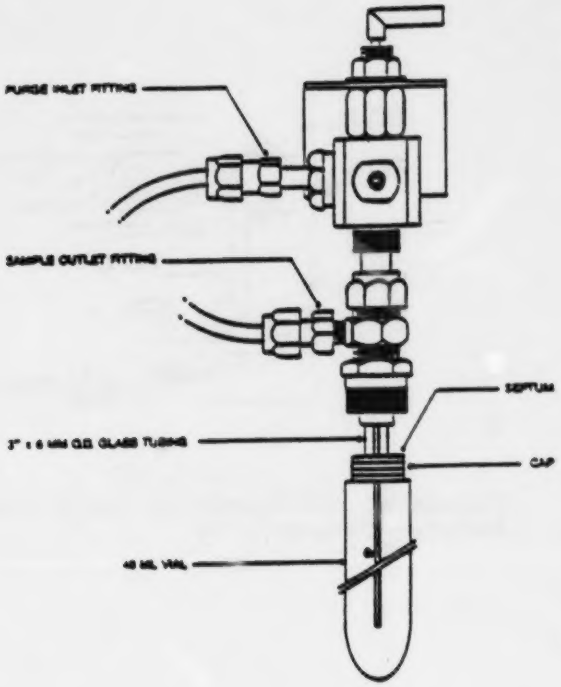

PURGE INLET FITTING
SAMPLE OUTLET FITTING
SEPTUM
3" x 6 MM O.D. GLASS TUBING
CAP
40 ML VIAL

Figure 2 Purging Device for Soils or Waters

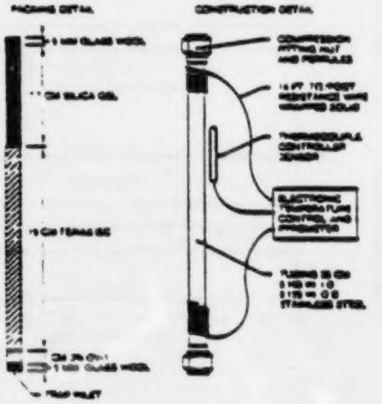

PACKING DETAIL
CONSTRUCTION DETAIL
5 MM GLASS WOOL
CM SILICA GEL
15 CM TENAX GC
1 CM 3% OV-1
5 MM GLASS WOOL
TRAP INLET
COMPRESSION FITTING NUT AND FERRULES
14 FT. 7Ω/FOOT RESISTANCE WIRE WRAPPED SOLID
THERMOCOUPLE/ CONTROLLER SENSOR
ELECTRONIC TEMPERATURE CONTROL AND PYROMETER
TUBING 25 CM 0.105 IN. I.D. 0.125 IN. O.D. STAINLESS STEEL

Figure 3 Trap Construction and Packings

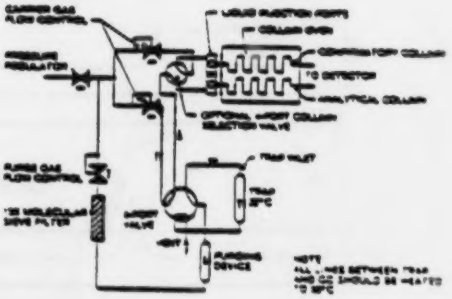

CARRIER GAS FLOW CONTROL
PRESSURE REGULATOR
LIQUID INJECTION PORTS
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN SELECTION VALVE
TRAP INLET
TRAP 22°C
PURGE GAS FLOW CONTROL
13X MOLECULAR SIEVE FILTER
6-PORT VALVE
VENT
PURGING DEVICE
NOTE:
ALL LINES BETWEEN TRAP AND GC SHOULD BE HEATED TO 80°C

Figure 4 Schematic of Purge and Trap Device--Purge Mode

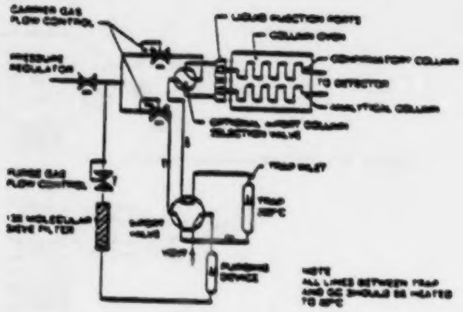

CARRIER GAS FLOW CONTROL
PRESSURE REGULATOR
LIQUID INJECTION PORTS
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN SELECTION VALVE
TRAP INLET
PURGE GAS FLOW CONTROL
13X MOLECULAR SIEVE FILTER
6-PORT VALVE
TRAP
VENT
PURGING DEVICE
NOTE ALL LINES BETWEEN TRAP AND GC SHOULD BE HEATED TO 80°C

Figure 5 Schematic of Purge and Trap Device--Desorb Mode

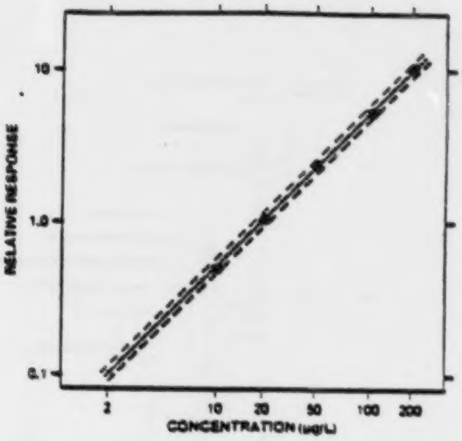


Figure 6 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a +/- 10 Percent Error Window.

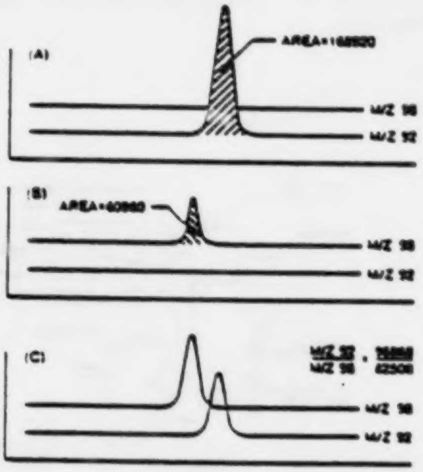


Figure 7 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene-d8, and (C) a Mixture of Toluene and Toluene-d8.

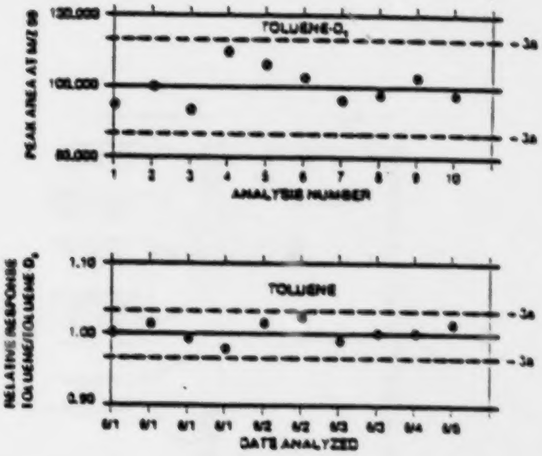
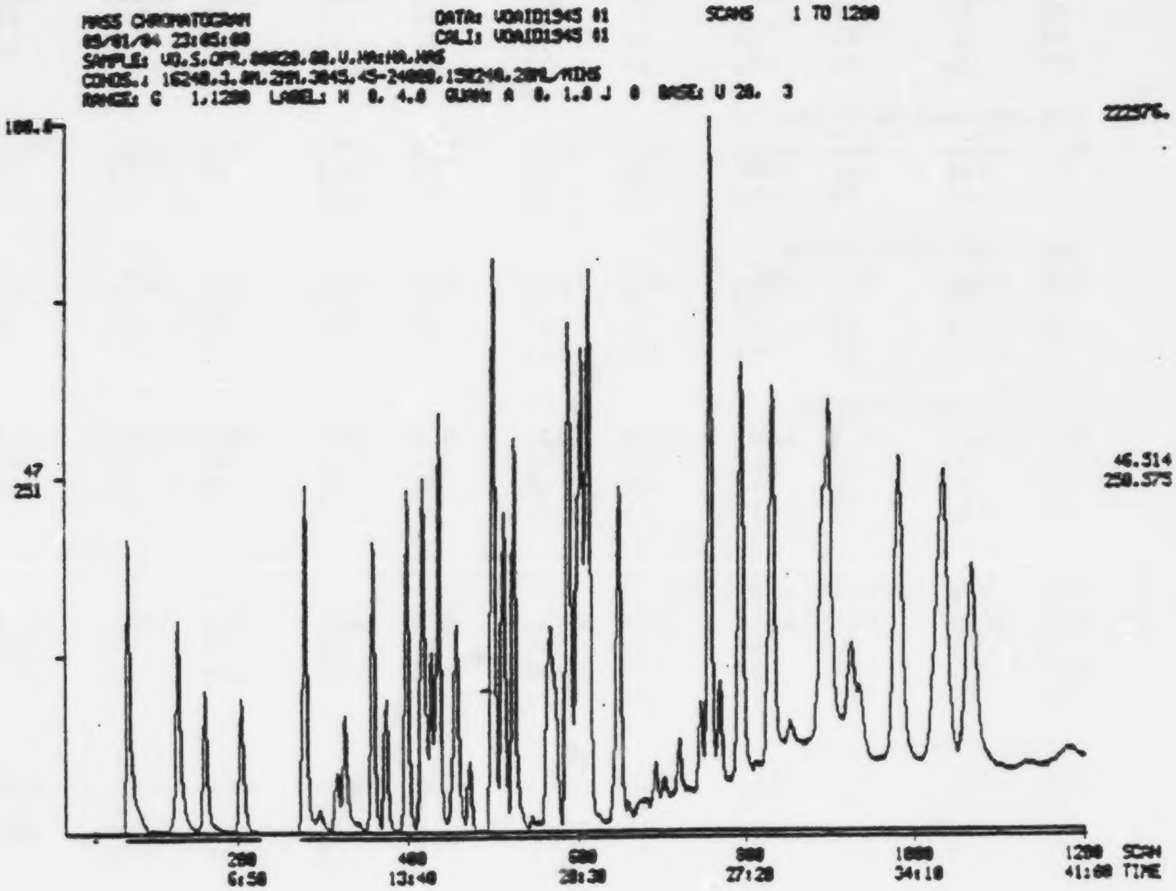


Figure 8 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene-d8 (lower graph) Plotted as a Function of Time or Analysis Number

Figure 9 Chromatogram of Aqueous Performance Standard



Appendix A: Mass Spectra in the Form of Mass/intensity Lists

532 allyl alcohol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	30	43	39	44	232	45	12	53	13	55	59
56	58	57	1000	58	300	61	15				

533 carbon disulfide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	282	46	10	64	14	76	1000	77	27	78	82

534 2-chloro-1,3-butadiene (chloroprene)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
48	21	49	91	50	223	51	246	52	241	53	1000
54	41	61	30	62	54	63	11	64	16	73	21
87	12	88	452	89	22	90	137				

535 chloroacetonitrile

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	135	48	1000	49	88	50	294	51	12	73	22
74	43	75	884	76	39	77	278				

536 3-chloropropene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
35	39	36	40	40	44	42	206	47	40	58	35
49	176	51	64	52	31	61	29	73	22	75	138
76	1000	77	74	78	324						

537 crotonaldehyde

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
35	26	40	28	42	339	43	48	44	335	49	27
50	40	51	20	52	21	53	31	55	55	68	24
69	511	70	1000	71	43						

538 1,2-dibromoethane (EDB)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
79	50	80	13	31	51	82	15	93	54	95	42
105	32	106	29	107	1000	108	38	109	922	110	19
186	13	188	27	190	13						

539 dibromomethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
43	99	44	101	45	30	79	184	80	35	81	175
91	142	92	61	93	1000	94	64	95	875	160	18
172	375	173	14	174	719	175	12	176	342		

540 trans-1,4-dichloro-2-butene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	166	50	171	51	289	52	85	53	878	54	273
62	286	64	91	75	1000	77	323	88	246	89	415
90	93	91	129	124	138	126	86	128	12		

541 1,3-dichloropropane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	15	42	44	47	19	48	20	49	193	51	55
61	18	62	22	63	131	65	38	75	47	76	1000
77	46	78	310	79	12						

542 cis-1,3-dichloropropene

37	262	38	269	39	998	49	596	51	189	75	1000
77	328	110	254	112	161						

543 ethyl cyanide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	115	50	34	51	166	52	190	53	127	54	1000
55	193										

544 ethyl methacrylate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	127	43	48	45	155	55	32	58	39	68	60
69	1000	70	83	71	25	85	14	86	169	87	21
96	17	99	93	113	11	114	119				

545 2-hexanone (methyl butyl ketone)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	61	43	1000	44	24	55	12	57	130	58	382
59	21	71	36	85	37	100	56				

546 iodomethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	57	127	328	128	17	139	39	140	34	141	120
142	1000	143	12								

547 isobutyl alcohol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
34	21	35	13	36	13	37	11	39	10	42	575
43	1000	44	42	45	21	55	40	56	37	57	21
59	25	73	12	74	63						

548 methacrylonitrile

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
38	24	39	21	41	26	42	100	49	19	50	60
51	214	52	446	53	19	62	24	63	59	64	136
65	55	66	400	67	1000	68	51				

549 methyl methacrylate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	127	43	52	45	48	53	30	55	100	56	49
59	124	68	28	69	1000	70	51	82	26	85	45
98	20	99	89	100	442	101	22				

550 4-methyl-2-pentanone (methyl isobutyl ketone; MIBK)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	69	43	1000	44	54	53	11	55	15	56	13
57	205	58	346	59	20	67	12	69	10	85	96
100	94										

551 1,1,1,2-tetrachloroethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	144	49	163	60	303	61	330	62	98	82	45
84	31	95	416	96	152	97	270	98	84	117	804
121	236	131	1000	133	955	135	301				

552 trichlorofluoromethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	95	47	153	49	43	51	21	52	14	66	162
68	53	82	40	84	28	101	1000	102	10	103	671
105	102	117	16	119	14						

553 1,2,3-trichloropropane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	285	51	87	61	300	62	107	63	98	75	1000
76	38	77	302	83	23	96	29	97	166	98	20
99	103	110	265	111	28	112	164	114	25		

554 vinyl acetate

36	5	42	103	43	1000	44	70	45	8	86	57

EPA METHOD
NO. 1625C

31 October 1986 Draft

Method 1625, Revision C

Semivolatile Organic Compounds by Isotope Dilution GCMS

1 Scope and application

1.1 This method is designed to determine the semivolatile toxic organic pollutants associated with the 1976 Consent Decree; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation and Liability Act; and other compounds amenable to extraction and analysis by capillary column gas chromatography-mass spectrometry (GCMS).

1.2 The chemical compounds listed in tables 1 through 4 may be determined in waters, soils, and municipal sludges by this method. The method is designed to meet the survey requirements of the Environmental Protection Agency (EPA).

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits in tables 5 and 6 typify the minimum quantity that can be detected with no interferences present.

1.4 The GCMS portions of this method are for use only by analysts experienced with GCMS or under the close supervision of such qualified persons. Laboratories unfamiliar with analyses of environmental samples by GCMS should run the performance tests in reference 1 before beginning.

2 Summary of method

2.1 The percent solids content of a sample is determined.

Stable isotopically labeled analogs of the compounds of interest are added to the sample.

If the solids content is less than one percent, a one liter sample is extracted at pH 12 - 13, then at pH <2 with methylene chloride using continuous extraction techniques. If the solids content is 30 percent percent or less, the sample is diluted to one percent solids with reagent water, homogenized ultrasonically, and extracted at pH 12-13, then at pH <2 with methylene chloride using continuous extraction techniques. If the solids content is greater than 30 percent, the sample is extracted using ultrasonic techniques.

Each extract is dried over sodium sulfate, concentrated to a volume of five mL, cleaned up using gel permeation chromatography (GPC), if necessary, and concentrated to one mL. An internal standard is added to the extract, and a one uL aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated by GC and detected by a mass spectrometer (MS). The labeled compounds serve to correct the variability of the analytical technique.

2.2 Identification of a pollutant (qualitative analysis) is performed in one of three ways: (1) For compounds listed in tables 1 and 2, and for other compounds for which authentic standards are available, the GCMS system is calibrated and the mass spectrum and retention time for each standard are stored in a user created library. A compound is identified when its retention time and mass spectrum agree with the library retention time and spectrum. (2) For compounds listed in tables 3 and 4, and for other compounds for which standards are not available, a compound is identified when the retention time and mass spectrum spectrum agree with those specified in this method. (3) For chromatographic peaks which are not identified by (1) and (2) above, the background corrected spectrum at the peak maximum is compared with spectra in the EPA/NIH Mass Spectral File (reference 2). Tentative identification is established when the spectrum agrees.

2.3 Quantitative analysis is performed in one of four ways by GCMS using extracted ion current profile (EICP) areas: (1) For compounds listed in tables 1 and 2, and for other compounds for which standards and labeled analogs are available, the GCMS system is calibrated and the compound concentration is determined using an isotope dilution technique. (2) For compounds listed in tables 1 and 2, and for other compounds for which authentic standards but no labeled compounds are available, the GCMS system is calibrated and the compound concentration is determined using an internal standard technique. (3) For compounds listed in tables 3 and 4, and for other compounds for which standards are not available, compound concentrations are determined using known response factors. (4) For compounds for which neither standards nor known response factors are available, compound concentration is determined using the sum of the EICP areas relative to the sum of the EICP areas of the internal standard.

2.4 Quality is assured through reproducible calibration and testing of the extraction and GCMS systems.

3 Contamination and interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms and spectra. All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running method blanks initially and with each sample lot (samples started through the extraction process on a given 8 hr shift, to a maximum of 20). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Glassware and, where possible, reagents are cleaned by solvent rinse and baking at 450 °C for one hour minimum.

3.2 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled.

4 Safety

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 3 - 5.

4.2 The following compounds covered by this method have been tentatively classified as know or suspected human or mammalian carcinogens: benzo(a)anthracene, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, and beta-naphthylamine. Primary standards of these compounds shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

5 Apparatus and materials

5.1 Sampling equipment for discrete or composite sampling.

5.1.1 Sample Bottles and Caps

5.1.1.1 Liquid Samples (waters, sludges and similar materials that contain less than five percent solids)--Sample bottle, amber glass, 1.1 liters minimum, with screw cap.

5.1.1.2 Solid samples (soils, sediments, sludges, filter cake, compost, and similar materials that contain more than five percent solids)--Sample bottle, wide mouth, amber glass, 500 mL minimum.

5.1.1.3 If amber bottles are not available, samples shall be protected from light.

5.1.1.4 Bottle caps--threaded to fit sample bottles. Caps shall be lined with Teflon.

5.1.1.5 Cleaning

5.1.1.5.1 Bottles are detergent water washed, then solvent rinsed or baked at 450 °C for one hour minimum before use.

5.1.1.5.2 Liners are detergent water washed, then reagent water (section 6.5.1) and solvent rinsed, and baked at approx 200 °C for one hour minimum prior to use.

5.1.2 Compositing equipment--automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Sample containers are kept at 0 - 4 °C during sampling. Glass or Teflon tubing only shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water (section 6.5.1) to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

5.2 Equipment for determining percent moisture

5.2.1 Oven, capable of being temperature controlled at 110 +/- 5 °C.

5.2.2 Dessicator

5.3 Sonic disruptor--375 watt with pulsing capability and 3/4 in. disruptor horn (Ultrasonics, Inc, Model 375C, or equivalent).

5.4 Extraction apparatus

5.4.1 Continuous liquid-liquid extractor--Teflon or glass connecting joints and stopcocks without lubrication, 1.5 - 2 liter capacity (Hershberg-Wolf Extractor, Ace Glass 6841-10, or equivalent).

5.4.2 Beakers

5.4.2.1 1.5 - 2 liter, calibrated to one liter

5.4.2.2 400 - 500 mL

5.4.2.3 Spatulas--stainless steel

5.4.3 Filtration apparatus

5.4.3.1 Glass funnel--125 - 250 mL

5.4.3.2 Filter paper for above (Whatman 41, or equivalent)

5.5 Drying column--15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

5.6 Kuderna-Danish (K-D) apparatus

5.6.1 Concentrator tube--10mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

5.6.2 Evaporation flask--500 mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).

5.6.3 Snyder column--three ball macro (Kontes K-503000-0232, or equivalent).

5.6.4 Snyder column--two ball micro (Kontes K-469002-0219, or equivalent).

5.6.5 Boiling chips--approx 10/40 mesh, extracted with methylene chloride and baked at 450 °C for one hr minimum.

5.7 Water bath--heated, with concentric ring cover, capable of temperature control (+/- 2 °C), installed in a fume hood.

5.8 Sample vials--amber glass, 2 - 5 mL with Teflon-lined screw cap.

5.9 Balances

5.9.1 Analytical--capable of weighing 0.1 mg.

5.9.2 Top loading--capable of weighing 10 mg.

5.10 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Model GPC Autoprep 1002, or equivalent)

5.10.1 Column--600 - 700 mm x 25 mm i.d., packed with 70 g of SX-3 Bio-beads

5.11 Gas chromatograph--shall have splitless or on-column injection port for capillary column, temperature program with 30 °C hold, and shall meet all of the performance specifications in section 12.

5.11.1 Column--30 +/-5 m x 0.25 +/- 0.02 mm i.d. 5% phenyl, 94% methyl, 1% vinyl silicone bonded phase fused silica capillary column (J & W DB-5, or equivalent).

5.12 Mass spectrometer--70 eV electron impact ionization, shall repetitively scan from 35 to 450 amu in 0.95 - 1.00 second, and shall produce a unit resolution (valleys between m/z 441-442 less than 10 percent of the height of the 441 peak), background corrected mass spectrum from 50 ng decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet. The spectrum shall meet the mass-intensity criteria in table 7 (reference 6). The mass spectrometer shall be interfaced to the GC such that the end of the capillary column terminates within one centimeter of the ion source but does not intercept the electron or ion beams. All portions of the column which connect the GC to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

5.13 Data system--shall collect and record MS data, store mass-intensity data in spectral libraries, process GCMS data, generate reports, and shall compute and record response factors.

5.13.1 Data acquisition--mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

5.13.2 Mass spectral libraries--user created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse search GCMS runs for the compounds of interest (section 7.2).

5.13.3 Data processing--the data system shall be used to search, locate, identify, and quantify the compounds of interest in each GCMS analysis. Software routines shall be employed to compute retention times and peak areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

5.13.4 Response factors and multipoint calibrations--the data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multi-point calibration curves (section 7). Computations of relative standard deviation (coefficient of variation) are used for testing calibration linearity. Statistics on initial (section 8.2) and on-going (section 12.7) performance shall be computed and maintained.

6 Reagents and standards

6.1 Reagents for adjusting sample pH

6.1.1 Sodium hydroxide--reagent grade, 6N in reagent water.

6.1.2 Sulfuric acid--reagent grade, 6N in reagent water.

6.2 Sodium sulfate--reagent grade, granular anhydrous, rinsed with methylene chloride (20 mL/g), baked at 450 °C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering.

6.3 Methylene chloride--distilled in glass (Burdick and Jackson, or equivalent).

6.4 GPC calibration solutions

6.4.1 Corn oil--200 mg/mL in methylene chloride

6.4.2 Bis(2-ethylhexyl)phthalate) and pentachlorophenol--4.0 mg/mL each in methylene chloride

6.5 Reference matrices

6.5.1 Reagent water--water in which the compounds of interest and interfering compounds are not detected by this method.

6.5.2 High solids reference matrix--playground sand or similar material in which the compounds of interest and interfering compounds are not detected by this method.

6.6 Standard solutions--purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at -20 to -10 °C in screw-capped vials with Teflon-lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. The vials are brought to room temperature prior to use. Any precipitate is redissolved and solvent is added if solvent loss has occurred.

6.7 Preparation of stock solutions--prepare in methylene chloride, benzene, p-dioxane, or a mixture of these solvents per the steps below. Observe the safety precautions in section 4. The large number of labeled and unlabeled acid and base/neutral compounds used for combined calibration (section 7) and calibration verification (12.5) require high concentrations (approx 40 mg/mL) when individual stock solutions are prepared, so that dilutions of mixtures will permit calibration with all compounds in a single set of solutions. The working range for most compounds is 10-200 ug/mL. Compounds with a reduced MS response may be prepared at higher concentrations.

6.7.1 Dissolve an appropriate amount of assayed reference material in a suitable solvent. For example, weigh 400 mg naphthalene in a 10 mL ground glass stoppered volumetric flask and fill to the mark with benzene. After the naphthalene is completely dissolved, transfer the solution to a 15 mL vial with Teflon-lined cap.

6.7.2 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Qaulity control check samples that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.7.3 Stock standard solutions shall be replaced after six months, or sooner if comparison with quality control check standards indicates a change in concentration.

6.8 Labeled compound spiking solution--from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution at a concentration of 200 ug/mL, or at a concentration appropriate to the MS response of each compound.

6.9 Secondary standard--using stock solutions (section 6.7), prepare a secondary standard containing all of the compounds in tables 1 and 2 at a concentration of 400 ug/mL, or higher concentration appropriate to the MS response of the compound.

6.10 Internal standard solution--prepare 2,2'-difluorobiphenyl (DFB) at a concentration of 10 mg/mL in benzene.

6.11 DFTPP solution--prepare at 50 ug/mL in acetone.

6.12 Solutions for obtaining authentic mass spectra (section 7.2)--prepare mixtures of compounds at concentrations which will assure authentic spectra are obtained for storage in libraries.

6.13 Calibration solutions--combine 0.5 mL of the solution in section 6.8 with 25, 50, 125, 250, and 500 uL of the solution in section 6.9 and bring to 1.00 mL total volume each. This will produce calibration solutions of nominal 10, 20, 50, 100 and 200 ug/mL of the pollutants and a constant nominal 100 ug/mL of the labeled compounds. Spike each solution with 10 uL of the internal standard solution (section 6.10). These solutions permit the relative response (labeled to unlabeled) to be measured as a function of concentration (section 7.4).

6.14 Precision and recovery standard--used for determination of initial (section 8.2) and on-going (section 12.7) precision and recovery. This solution shall contain the pollutants and labeled compounds at a nominal concentration of 100 ug/mL.

6.15 Stability of solutions--all standard solutions (sections 6.8 - 6.14) shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if the peak area at the quantitation mass relative to the DFB internal standard remains within +/- 15 percent of the area obtained in the initial analysis of the standard.

7 Calibration

7.1 Assemble the GCMS and establish the operating conditions in table

5. Analyze standards per the procedure in section 11 to demonstrate that the analytical system meets the minimum levels in tables 5 and 6, and the mass-intensity criteria in table 7 for 50 ng DFTPP.

7.2 Mass spectral libraries--detection and identification of compounds of interest are dependent upon spectra stored in user created libraries.

7.2.1 Obtain a mass spectrum of each pollutant, labeled compound, and the internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound.

7.2.2 Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic masses or introduce other distortion.

7.2.3 The authentic reference spectrum is obtained under DFTPP tuning conditions (section 7.1 and table 7) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. The spectrum may be further edited to remove common interfering masses. If 5 mass spectral peaks cannot be obtained under the scan conditions given in section 5.12, the mass spectrometer may be scanned to an m/z lower than 35 to gain additional spectral information. The spectrum obtained is stored for reverse search and for compound confirmation.

7.2.5 For the compounds in tables 3 and 4 and for other compounds for which the mass spectra, quantitation m/z's, and retention times are known but the instrument is not to be calibrated, add the retention time and reference compound (tables 5 and 6); the responsefactor and the quantitation m/z (tables 8 and 9); and spectrum (Appendix A) to the reverse search library. Edit the spectrum per section 7.2.4, if necessary.

7.3 Analytical range--demonstrate that 20 ng anthracene or phenanthrene produces an area at m/z 178 approx one-tenth that required to exceed the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required, and to diagnose instrument sensitivity problems (section 15.3). The 20 ug/mL calibration standard (section 6.13) can be used to demonstrate this performance.

7.3.1 Polar compound detection--demonstrate that unlabeled pentachlorophenol and benzidine are detectable at the 50 ug/mL level (per all criteria in section 13). The 50 ug/mL calibration standard (section 6.13) can be used to demonstrate this performance.

7.4 Calibration with isotope dilution--isotope dilution is used when 1) labeled compounds are available, 2) interferences do not preclude its use, and 3) the quantitation m/z (tables 8 and 9) extracted ion current profile (EICP) area for the compound is in the calibration range. Alternate labeled compounds and quantitation m/z's may be used based on availability. If any of the above conditions preclude isotope dilution, the internal standard method (section 7.5) is used.

7.4.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (pollutant to labeled) vs concentration in standard solutions is plotted or computed using a linear regression. The example in Figure 1 shows a calibration curve for phenol using phenol-d5 as the isotopic diluent. Also shown are the +/- 10 percent error limits (dotted lines). Relative Response (RR) is determined according to the procedures described below. A minimum of five data points are employed for calibration.

7.4.2 The relative response of a pollutant to its labeled analog is determined from isotope ratio values computed from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured for the pure pollutant.

R_y = the isotope ratio measured for the labeled compound.

R_m = the isotope ratio of an analytical mixture of pollutant and labeled compounds.

The m/z's are selected such that $R_x > R_y$. If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by the internal standard method.

7.4.3 Capillary columns usually separate the pollutant-labeled pair, with the labeled compound eluted first (figure 2). For this case,

R_x = [area m_1/z]/1, at the retention time of the pollutant (RT_2).

R_y = 1/[area m_2/z], at the retention time of the labeled compound RT_1)

R_m = [area at m_1/z (at RT_2)]/[area at m_2/z (at RT_1)], as measured in the mixture of the pollutant and labeled compounds (figure 2), and RR = R_m.

7.4.4 Special precautions are taken when the pollutant-labeled pair is not separated, or when another labeled compound with interfering spectral masses overlaps the pollutant (a case which can occur with isomeric compounds). In this case, it is necessary to determine the respective contributions of the pollutant and labeled compounds to the respective EICP areas. If the peaks are separated well enough to permit the data system or operator to remove the contributions of the compounds to each other, the equations in section 7.4.3 apply. This usually occurs when the height of the valley between the two GC peaks at the same m/z is less than 10 percent of the height of the shorter of the two peaks. If significant GC and spectral overlap occur, RR is computed using the following equation:

$RR = (R_y - R_m)(R_x + 1)/(R_m - R_x)(R_y + 1)$, where R_x is measured as shown in figure 3A, R_y is measured as shown in figure 3B, and R_m is measured as shown in figure 3C. For the example, $R_x = 46100/4780 = 9.644$, $R_y = 2650/43600 = 0.0608$, $R_m = 49200/48300 = 1.019$, and $RR = 1.114$.

7.4.5 To calibrate the analytical system by isotope dilution, analyze a 1.0 uL aliquot of each of the calibration standards (section 6.13) using the procedure in section 11. Compute the RR at each concentration.

7.4.6 Linearity--if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the 5 point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point calibration range.

7.5 Calibration by internal standard--used when criteria for isotope dilution (section 7.4) cannot be met. The internal standard to be used for both acid and base/neutral analyses is 2,2'-difluorobiphenyl. The internal standard method is also applied to determination of compounds having no labeled analog, and to measurement of labeled compounds for intra-laboratory statistics (sections 8.4 and 12.7.4).

7.5.1 Response factors--calibration requires the determination of response factors (RF) which are defined by the following equation: $RF = (A_s \times C_{is})/(A_{is} \times C_s)$, where

A_s is the area of the characteristic mass for the compound in the daily standard

A_{is} is the area of the characteristric mass for the internal standard

C_{is} is the concentration of the internal standard (ug/mL)

C_s is the concentration of the compound in the daily standard (ug/mL)

7.5.1.1 The response factor is determined for at least five concentrations appropriate to the response of each compound (section 6.13); nominally, 10, 20, 50, 100, and 200 ug/mL. The amount of internal standard added to each extract is the same (100 ug/mL) so that C_{is} remains constant. The RF is plotted vs concentration for each compound in the standard (C_s) to produce a calibration curve.

7.5.1.2 Linearity--if the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

7.6 Combined calibration--by using calibration solutions (section 6.13) containing the pollutants, labeled compounds, and the internal standard, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (section 12.5) by analyzing the 100 ug/mL calibration standard (section 6.13). Recalibration is required only if calibration verification (section 12.5) criteria cannot be met.

8 Quality assurance/quality control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program (reference 7). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

If the method is to be applied routinely to samples containing high solids with very little moisture (e.g., soils, filter cake, compost), the high solids reference matrix (section 6.5.2) is substituted for the reagent water (6.5.1) in all performance tests, and the high solids method (section 10) is used for these tests.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in section 8.2.

8.1.2 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in section 8.2 to demonstrate method performance.

8.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in section 8.5.

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (section 15).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (section 6.14) that the analysis system is in control. These procedures are described in sections 12.1, 12.5, and 12.7.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in section 8.4.

8.2 Initial precision and accuracy--to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.2.1 For low solids (aqueous samples), extract, concentrate, and analyze two sets of four one-liter aliquots (8 aliquots total) of the precision and recovery standard (section 6.14) according to the procedure in section 10. For high solids samples, two sets of four 30 gram aliquots of the high solids reference matrix are used.

8.2.2 Using results of the first set of four analyses, compute the average recovery (X) in ug/mL and the standard deviation of the recovery (s) in ug/mL for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

8.2.3 For each compound, compare s and X with the corresponding limits for initial precision and accuracy in table 10. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 10 present a substantial probability that one or more will fail the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.4 Using the results of the second set of four analyses, compute s and X for only those compounds which failed the test of the first set of four analyses (section 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for these compounds. In this event, correct the problem and repeat the entire test (section 8.2.1).

8.3 The laboratory shall spike all samples with labeled compounds to assess method performance on the sample matrix.

8.3.1 Analyze each sample according to the method beginning in section 10.

8.3.2 Compute the percent recovery (P) of the labeled compounds using the internal standard method (section 7.5).

8.3.3 Compare the labeled compound recovery for each compound with the corresponding limits in table 10. If the recovery of any compound falls outside its warning limit, method performance is unacceptable for that compound in that sample. Therefore, the sample is complex. Water samples are diluted, and smaller amounts of soils, sludges, and sediments are reanalyzed per section 15.

8.4 As part of the QA program for the laboratory, method accuracy for samples shall be assessed and records shall be maintained. After the analysis of five samples or a given matrix type (water, soil, sludge, sediment) for which the labeled compounds pass the tests in section 8.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$ for each matrix. For example, if $P = 90\%$ and $s_p = 10\%$ for five analyses of compost, the accuracy interval is expressed as 70 - 110%. Update the accuracy assessment for each compound in each matrix on a regular basis (e.g. after each 5 - 10 new accuracy measurements).

8.5 Blanks--reagent water and high solids reference matrix blanks are analyzed to demonstrate freedom from contamination.

8.5.1 Extract and concentrate a one liter reagent water blank or a high solids reference matrix blank with each sample lot (samples started through the extraction process on the same 8 hr shift, to a maximum of 20 samples). Analyze the blank immediately after analysis of the precision and recovery standard (section 6.14) to demonstrate freedom from contamination.

8.5.2 If any of the compounds of interest (tables 1 thru 4) or any potentially interfering compound is found in an aqueous blank at greater than 10 ug/L, or in a high solids reference matrix blank at greater than 100 ug/kg (assuming a response factor of 1 relative to the internal standard for compounds not listed in tables 1 thru 4), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

8.6 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (section 7), calibration verification (section 12.5), and for initial (section 8.2) and on-going (section 12.7) precision and recovery should be identical, so that the most precise results will be obtained. The GCMS instrument in particular will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of semi-volatiles by this method.

8.7 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

9 Sample collection, preservation, and handling

9.1 Collect samples in glass containers following conventional sampling practices (reference 8). Aqueous samples which flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide mouth jars.

9.2 Maintain samples at 0 - 4 °C from the time of collection until extraction. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. EPA methods 330.4 and 330.5 may be used to measure residual chlorine (reference 9).

9.3 Begin sample extraction within seven days of collection, and analyze all extracts within 40 days of extraction.

10 Sample extraction, concentration, and cleanup--samples containing one percent solids or less are extracted directly using continuous liquid/liquid extraction techniques (section 10.2.1 and figure 4). Samples containing one to 30 percent solids are diluted to the one percent level with reagent water (section 10.2.2) and extracted using continuous liquid/liquid extraction techniques. Samples containing greater than 30 percent solids are extracted using ultrasonic techniques (section 10.2.5)

10.1 Determination of percent solids

10.1.1 Weigh 5 - 10 g of sample into a tared beaker.

10.1.2 Dry overnight (12 hours minimum) at 110 +/- 5 °C, and cool in a dessicator.

10.1.3 Determine percent solids as follows:

$$\% \text{ solids} = \frac{\text{weight of dry sample}}{\text{weight of wet sample}} \times 100$$

10.2 Preparation of samples for extraction

10.2.1 Samples containing one percent solids or less--extract sample directly using continuous liquid/liquid extraction techniques.

10.2.1.1 Measure 1.00 +/- 0.01 liter of sample into a clean 1.5 - 2.0 liter beaker.

10.2.1.2 Dilute aliquot--for samples which are expected to be difficult to extract, concentrate, or clean-up, measure an additional 100.0 +/- 1.0 mL into a clean 1.5 - 2.0 liter beaker and dilute to a final volume of 1.00 +/- 0.1 liter with reagent water.

10.2.1.3 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into the sample aliquots. Proceed to preparation of the QC aliquots for low solids samples (section 10.2.3).

10.2.2 Samples containing one to 30 percent solids

10.2.2.1 Mix sample thoroughly.

10.2.2.2 Using the percent solids found in 10.1.3, determine the weight of sample required to produce one liter of solution containing one percent solids as follows:

$$\text{sample weight} = \frac{1000}{\%\ \text{solids}}\ \text{grams}$$

10.2.2.3 Place the weight determined in 10.2.2.2 in a clean 1.5 - 2.0 liter beaker. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

10.2.2.4 Dilute aliquot--for samples which are expected to be difficult to extract, concentrate, or clean-up, weigh an amount of sample equal to one-tenth the amount determined in 10.2.2.2 into a second clean 1.5 - 2.0 liter beaker. When diluted to 1.0 liter, this dilute aliquot will contain 0.1 percent solids.

10.2.2.5 Bring the sample aliquot(s) above to 100 - 200 mL volume with reagent water.

10.2.2.6 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into each sample aliquot.

10.2.2.7 Using a clean metal spatula, break any solid portions of the sample into small pieces.

10.2.2.8 Place the 3/4 in. horn on the ultrasonic probe approx 1/2 in. below the surface of each sample aliquot and pulse at 50 percent for three minutes at full power. If necessary, remove the probe from the solution and break any large pieces using the metal spatula or a stirring rod and repeat the sonication. Clean the probe with methylene chloride:acetone (1:1) between samples to preclude cross-contamination.

10.2.2.9 Bring the sample volume to 1.0 +/- 0.1 liter with reagent water.

10.2.3 Preparation of QC aliquots for samples containing low solids

(<30 percent).

10.2.3.1 For each sample or sample lot (to a maximum of 20) to be extracted at the same time, place three 1.0 +/- 0.01 liter aliquots of reagent water in clean 1.5 - 2.0 liter beakers.

10.2.3.2 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into one reagent water aliquot. This aliquot will serve as the blank.

10.2.3.3 Spike 1.0 mL of the precision and recovery standard (section 6.14) into the two remaining reagent water aliquots.

10.2.4 Stir and equilibrate all sample and QC solutions for 1 - 2 hours. Extract the samples and QC aliquots per section 10.3.

10.2.5 Samples containing 30 percent solids or greater

10.2.5.1 Mix the sample thoroughly

10.2.5.2 Weigh 30 +/- 0.3 grams into a clean 400 - 500 mL beaker. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

10.2.5.3 Dilute aliquot--for samples which are expected to be difficult to extract, concentrate, or clean-up, weigh 3 +/- 0.03 grams into a clean 400 - 500 mL beaker.

10.2.5.4 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into each sample aliquot.

10.2.5.5 QC aliquots--for each sample or sample lot (to a maximum of 20) to be extracted at the same time, place three 30 +/- 0.3 gram aliquots of the high solids reference matrix in clean 400 - 500 mL beakers.

10.2.5.6 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into one high solids reference matrix aliquot. This aliquot will serve as the blank.

10.2.5.7 Spike 1.0 mL of the precision and recovery standard (section

6.14) into the two remaining high solids reference matrix aliquots. Extract, concentrate, and clean up the high solids samples per sections 10.4 through 10.8.

10.3 Continuous extraction of low solids (aqueous) samples--place 100 - 150 mL methylene chloride in each continuous extractor and 200 - 300 mL in each distilling flask.

10.3.1 Pour the sample(s), blank, and standard aliquots into the extractors. Rinse the glass containers with 50 - 100 mL methylene chloride and add to the respective extractors. Include all solids in the extraction process.

10.3.2 Base/neutral extraction--adjust the pH of the waters in the extractors to 12 - 13 with 6N NaOH while monitoring with a pH meter. Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1 - 2 drops of methylene chloride per second will fall from the condensor tip into the water. Test and adjust the pH of the waters during the first 1 - 2 hr and during the fifth to tenth hr of extraction. Extract for 24 - 48 hours.

10.3.3 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a drying column containing 7 to 10 cm anhydrous sodium sulfate. Rinse the distilling flask with 30 - 50 mL of methylene chloride and pour through the drying column. Collect the solution in a 500 mL K-D evaporator flask equipped with a 10 mL concentrator tube. Seal, label as the base/neutral fraction, and concentrate per sections 10.5 to 10.6.

10.3.4 Acid extraction--adjust the pH of the waters in the extractors to 2 or less using 6N sulfuric acid. Charge clean distilling flasks with 300 - 400 mL of methylene chloride. Test and adjust the pH of the waters during the first 1 - 2 hr and during the fifth to tenth hr of extraction. Extract for 24 - 48 hours. Repeat section 10.3.3, except label as the acid fraction.

10.4 Ultrasonic extraction of high solids samples

10.4.1 Add 60 grams of anhydrous sodium sulfate the sample and QC aliquot(s) (section 10.2.5) and mix thoroughly.

10.4.2 Add 100 +/- 10 mL of acetone:methylene chloride (1:1) to the sample and mix thoroughly.

10.4.3 Place the 3/4 in. horn on the ultrasonic probe approx 1/2 in. below the surface of the solvent but above the solids layer and pulse at 50 percent for three minutes at full power. If necessary, remove the probe from the solution and break any large pieces using the metal spatula or a stirring rod and repeat the sonication.

10.4.4 Decant the extracts through Whatman 41 filter paper using glass funnels and collect in 500 - 1000 mL graduated cylinders.

10.4.5 Repeat the extraction steps (10.4.2 - 10.4.4) twice more for each sample and QC aliquot. On the final extraction, swirl the sample or QC aliquot, pour into its respective glass funnel, and rinse with acetone:methylene chloride. Record the total extract volume.

10.4.6 Pour each extract through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Rinse the graduated cylinder with 30 - 50 mL of methylene chloride and pour through the drying column. Collect each extract in a 500 mL K-D evaporator flask equipped with a 10 mL concentrator tube. Seal and label as the high solids semi-volatile fraction. Concentrate and clean up the samples and QC aliquots per sections 10.5 through 10.8.

10.5 Macro concentration--concentrate the extracts in separate 500 mL K-D flasks equipped with 10 mL concentrator tubes.

10.5.1 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the column by adding approx one mL of methylene chloride through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lowers joint into the concentrator tube with 1 - 2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

10.5.2 For performance standards (sections 8.2 and 12.7) and for blanks (section 8.5), combine the acid and base/neutral extracts for each at this point. Do not combine the acid and base/neutral extracts for aqueous samples.

10.6 Micro-concentration--Add a clean boiling chip and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approx 0.5 mL methylene chloride through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature as required to complete the concentration in 5 - 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the liquid reaches an apparent volume of approx 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint into the concentrator tube with approx

0.2 mL of methylene chloride. Adjust the final volume to 5.0 mL if the extract is to be cleaned up by GPC, or to 1.0 mL if it has been cleaned up or does not require clean-up.

10.7 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid, and mark the level on the vial. Label with the sample number and fraction, and store in the dark at -20 to -10 °C until ready for analysis.

10.8 GPC setup and calibration

10.8.1 Column packing

10.8.1.1 Place 75 +/- 5 g of SX-3 Bio-beads in a 400 - 500 mL beaker.

10.8.1.2 Cover the beads and allow to swell overnight (12 hours minimum).

10.8.1.3 Transfer the swelled beads to the column and pump solvent through the column, from bottom to top, at 4.5 - 5.5 mL/min.

10.8.1.4 After purging the column with solvent for 1 - 2 hours, adjust the column head pressure to 7 - 10 psig, and purge for 4 - 5 hours to remove air from the column. Maintain a head pressure of 7 - 10 psig.

10.8.2 Column calibration

10.8.2.1 Load 5 mL of the corn oil solution into sample loop number one, and 5 mL of the phthalate/phenol solution into sample loop number two.

10.8.2.2 Inject the corn oil and collect approx 10 mL fractions at two minute intervals for 36 minutes.

10.8.2.3 Inject the phthalate/phenol mixture and collect 15 mL fractions for 60 minutes.

10.8.2.4 Determine the corn oil elution pattern gravimetrically (by evaporation of each fraction and weighing the residue), or by UV, IR, or other technique which will detect the corn oil.

10.8.2.5 Determine the phthalate/phenol elution pattern by GC, GCMS, UV, IR, or other technique which will detect these compounds.

10.8.2.6 Plot a normalized chromatogram of the corn oil and phthalate/phenol mixture.

10.8.2.7 Choose the "dump time" to allow >85 percent removal of the corn oil and >85 percent recovery of the phthalate.

10.8.2.8 Choose the "collect time" to extend at least 10 minutes past the elution of the phenol.

10.8.2.9 Verify the calibration with pentachlorophenol after every 20 extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85 percent. If calibration is not verified, the system shall be recalibrated using the corn oil and phthalate/phenol mixture.

10.9 Extract cleanup

10.9.1 Filter the extract or load through the filter holder to remove particulates. Load the 5.0 mL extract onto the column. The maximum capacity of the column is 0.5 - 1.0 gram. If necessary, split the extract into multiple aliquots to prevent column overload.

10.9.2 Elute the extract using the calibration data determined in 10.8.2. Collect the eluate in a clean 400 - 500 mL beaker.

10.9.3 Concentrate the cleaned up extract per section 10.5.

10.9.4 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

10.9.5 If a particularly dirty extract is encountered, a 5.0 mL methylene chloride blank shall be run through the system to check for carry-over.

10.9.6 Reconcentrate the extract to one mL and transfer to a screw-cap vial per sections 10.6 and 10.7.

11 GCMS analysis

11.1 Establish the operating conditions given in tables 5 or 6 for analysis of the base/neutral or acid extracts, respectively. For analysis of combined extracts (section 10.5.2 and 10.9.6), use the operating conditions in table 5.

11.2 Bring the concentrated extract (section 10.7) or standard (sections 6.13 - 6.14) to room temperature and verify that any precipitate has redissolved. Verify the level on the extract (sections 6.6 and 10.7) and bring to the mark with solvent if required.

11.3 Add the internal standard solution (section 6.10) to the extract (use 1.0 uL of solution per 0.1 mL of extract) immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly.

11.4 Inject a volume of the standard solution or extract such that 100 ng of the internal standard will be injected, using on-column or splitless injection. For 1 mL extracts, this volume will be 1.0 uL. Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the benzo(ghi)perylene or pentachlorophenol peak elutes for the base/neutral (or semi-volatile) or acid fraction, respectively. Return the column to the initial temperature for analysis of the next sample.

12 System and laboratory performance

12.1 At the beginning of each 8 hr shift during which analyses are performed, GCMS system performance and calibration are verified for all pollutants and labeled compounds. For these tests, analysis of the 100 ug/mL calibration standard (section 6.13) shall be used to verify all performance criteria. Adjustment and/or recalibration (per section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, and precision and recovery standards be analyzed.

12.2 DFTPP spectrum validity--inject 1 uL of the DFTPP solution (section 6.11) either separately or within a few seconds of injection of the standard (section 12.1) analyzed at the beginning of each shift. The criteria in table 7 shall be met.

12.3 Retention times--the absolute retention time of 2,2'-difluorobiphenyl shall be within the range of 1078 to 1248 seconds and the relative retention times of all pollutants and labeled compounds shall fall within the limits given in tables 5 and 6.

12.4 GC resolution--the valley height between anthracene and phenanthrene at m/z 178 (or the analogs at m/z 188) shall not exceed 10 percent of the taller of the two peaks.

12.5 Calibration verification--compute the concentration of each pollutant (tables 1 and 2) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the calibration data determined in section 7.

12.5.1 For each pollutant and labeled compound being tested, compare the concentration with the calibration verification limit in table 10. If all compounds meet the acceptance criteria, calibration has been verified and analysis of blanks, samples, and precision and recovery standards may proceed. If, however, any compound fails, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the test (section

12.1), or recalibrate (section 7).

12.6 Multiple peaks--each compound injected shall give a single, distinct GC peak.

12.7 On-going precision and accuracy.

12.7.1 Analyze the extract of one of the pair of precision and recovery standards (section 10) prior to analysis of samples from the same lot.

12.7.2 Compute the concentration of each pollutant (tables 1 and 2) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method.

12.7.3 For each pollutant and labeled compound, compare the concentration with the limits for on-going accuracy in table 10. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 10 present a substantial probability that one or more will fail when all compounds are analyzed. To determine if the extraction/concentration system is out of control or if the failure is caused by probability, proceed as follows:

12.7.3.1 Analyze the second aliquot of the pair of precision and recovery standards (section 10).

12.7.3.2 Compute the concentration of only those pollutants or labeled compounds that failed the previous test (section 12.7.3). If these compounds now pass, the extraction/concentration processes are in control and analysis of blanks and samples may proceed. If, however, any of the same compounds fail again, the extraction/concentration processes are not being performed properly for these compounds. In this event, correct the problem, re-extract the sample lot (section 10) and repeat the on-going precision and recovery test (section 12.7).

12.7.4 Add results which pass the specifications in section 12.7.3 to initial and previous on-going data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance (Figure 5). Develop a statement of laboratory accuracy for each pollutant and labeled compound in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy as a recovery interval from R - $2s_r$ to R + $2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85 - 105%.

13 Qualitative determination--identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the mass spectral libraries. For compounds for which the relative retention times and mass spectra are known, identification is confirmed per sections 13.1 and 13.2. For unidentified GC peaks, the spectrum is compared to spectra in the EPA/NIH mass spectral file per section 13.3.

13.1 Labeled compounds and pollutants having no labeled analog (tables 1 thru 4):

13.1.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

13.1.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

13.1.3 For the compounds for which the system has been calibrated (tables 1 and 2), the retention time shall be within the windows specified in tables 5 and 6, or within +/- 15 scans or +/- 15 seconds (whichever is greater) for compounds for which no window is specified.

13.1.4 For the compounds for which the system has not been calibrated but the relative retention times and mass spectra are known (tables 3 and 4), the retention time relative to the 2,2'-difluorobiphenyl internal standard shall be within +/- 30 scans or +/- 30 seconds (whichever is greater) based on the nominal retention time specified in tables 5 and 6.

13.2 Pollutants having a labeled analog (tables 1 and 2):

13.2.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

13.2.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two for all masses stored in the spectral library.

13.2.3 The relative retention time between the pollutant and its labeled analog shall be within the windows specified in tables 5 and 6.

13.3 Unidentified GC peaks

13.3.1 The signals for masses specific to a GC peak shall all maximize within +/- 1 scan.

13.3.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two with the masses stored in the EPA/NIH Mass Spectral File.

13.4 M/z's present in the experimental mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the experimental mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (section 1.4) is to determine the presence or absence of the compound.

14 Quantitative determination

14.1 Isotope dilution--by adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon extraction, concentration, and gas chromatography. Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the phenol example given in figure 1 (section 7.4.1), RR would be equal to 1.114. For this RR value, the phenol calibration curve given in figure 1 indicates a concentration of 27 ug/mL in the sample extract (C_{ex}).

14.2 Internal standard--compute the concentration in the extract using the response factor determined from calibration data (section 7.5) and the following equation:

C_{ex} (ug/mL) = $(A_s \times C_{is})/(A_{is} \times RF)$

where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in section 7.5.1.

14.3 The concentration of the pollutant in the solid phase of the sample is computed using the concentration of the pollutant in the extract and the weight of the solids (section 10), as follows:

Concentration in solid (ug/kg) = $(C_{ex} \times V_{ex})/W_s$

where C_{ex} is the extract volume in mL and W_s is the sample weight in kg.

14.4 If the EICP area at the quantitation m/z for any compound exceeds the calibration range of the system, the extract of the dilute aliquot (section 10) is analyzed by isotope dilution; otherwise, the extract is diluted by a factor of 10, 9 uL of internal standard solution (section 6.10) are added to a 1.0 mL aliquot, and this diluted extract is analyzed by the internal standard method (section 14.2).

14.5 For GC peaks which are to be identified (per section 13.3), the sample is diluted by successive factors of 10 when any peak in the uncorrected mass spectrum at the GC peak maximum is saturated.

14.6 Results are reported for all pollutants, labeled compounds, and tentatively identified compounds found in all standards, blanks, and samples, in units of ug/L for aqueous samples or in ug/kg dry weight of solids for high solids samples (soils, sediments, filter cake, compost), to three significant figures. Results for samples which have been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 14.4) or at which no m/z in the spectrum is saturated (section 14.5). For compounds having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 14.4) and the labeled compound recovery is within the normal range for the method (section 15.4).

15 Analysis of complex samples

15.1 Some samples may contain high levels (>1000 ug/L) of the compounds of interest, interfering compounds, and/or polymeric materials. Some samples will not concentrate to one mL (section 10.6); others will overload the GC column and/or mass spectrometer.

15.2 Analyze the dilute aliquot (section 10) when the sample will not concentrate to 1.0 mL. If a dilute aliquot was not extracted, and the sample holding time (section 9.3) has not been exceeded, dilute an aliquot of an aqueous sample with reagent water, or weigh a dilute aliquot of a high solids sample and re-extract (section 10); otherwise, dilute the extract (section 14.4) and analyze by the internal standard method (section 14.2).

15.3 Recovery of internal standard--the EICP area of the internal standard should be within a factor of two of the area in the shift standard (section 12.1). If the absolute areas of the labeled compounds are within a factor of two of the respective areas in the shift standard, and the internal standard area is less than one-half of its respective area, then internal standard loss in the extract has occurred. In this case, use one of the labeled compounds (preferably a polynuclear aromatic hydrocarbon) to compute the concentration of a pollutant with no labeled analog.

15.4 Recovery of labeled compounds--in most samples, labeled compound recoveries will be similar to those from reagent water or from the high solids reference matrix (section 12.7). If the labeled compound recovery is outside the limits given in table 10, the extract from the dilute aliquot (section 10) is analyzed as in section 14.4. If the recoveries of all labeled compounds and the internal standard are low (per the criteria above), then a loss in instrument sensitivity is the most likely cause. In this case, the 100 ug/mL calibration standard (section 12.1) shall be analyzed and calibration verified (section 12.5). If a loss in sensitivity has occurred, the instrument shall be repaired, the performance specifications in section 12 shall be met, and the extract reanalyzed. If a loss in instrument sensitivity has not occurred, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

16 Method performance

16.1 Interlaboratory performance for this method is detailed in reference 10. Reference mass spectra, retention times, and response factors are from references 11 and 12. Results of initial tests of this method on municipal sludge can be found in reference 13.

16.2 A chromatogram of the 100 ug/mL acid/base/neutral calibration standard (section 6.13) is shown in figure 6.

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Table 1

Base/Neutral Extractable Compounds Determined by Calibrated GCMS Using Isotope Dilution and Internal Standard Techniques

	Pollutant				Labeled Compound		
Compound	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
acenaphthene	34205	83-32-9	001 B	001 B	d10	15067-20-2	201 B
acenaphthylene	34200	208-96-8	077 B	002 B	d8	93951-97-4	277 B
anthracene	34220	120-12-7	078 B	003 B	d10	1719-06-8	278 B
benzidine	39120	92-87-5	005 B	004 B	d8	92890-63-6	205 B
benzo(a)anthracene	34526	56-55-3	072 B	005 B	d12	1718-53-2	272 B
benzo(b)fluoranthene	34230	205-99-2	074 B	007 B	d12	93951-98-5	274 B
benzo(k)fluoranthene	34242	207-08-9	075 B	009 B	d12	93952-01-3	275 B
benzo(a)pyrene	34247	50-32-8	073 B	006 B	d12	63466-71-7	273 B
benzo(ghi)perylene	34521	191-24-2	079 B	008 B	d12	93951-66-7	279 B
biphenyl (Appendix C)	81513	92-52-4	512 B		d10	1486-01-7	612 B
bis(2-chloroethyl) ether	34273	111-44-4	018 B	011 B	d8	93952-02-4	218 B
bis(2-chloroethoxy)methane	34278	111-91-1	043 B	010 B	d8	93966-78-0	243 B
bis(2-chloroisopropyl) ether	34283	108-60-1	042 B	012 B	d12	93951-67-8	242 B
bis(2-ethylhexyl) phthalate	39100	117-81-7	066 B	013 B	d4	93951-87-2	266 B
4-bromophenyl phenyl ether	34636	101-55-3	041 B	014 B	d5	93951-83-8	241 B
butyl benzyl phthalate	34292	85-68-7	067 B	015 B	d4	93951-88-3	267 B
n-C10 (Appendix C)	77427	124-18-5	517 B		d22	16416-29-8	617 B
n-C12 (Appendix C)	77588	112-40-3	506 B		d26	16416-30-1	606 B
n-C14 (Appendix C)	77691	629-59-4	518 B				618 B
n-C16 (Appendix C)	77757	544-76-3	519 B		d34	15716-08-2	619 B
n-C18 (Appendix C)	77804	593-45-3	520 B				620 B
n-C20 (Appendix C)	77830	112-95-8	521 B		d42	62369-67-9	621 B
n-C22 (Appendix C)	77859	629-97-0	522 B				622 B
n-C24 (Appendix C)	77886	646-31-1	523 B		d50	16416-32-3	623 B
n-C26 (Appendix C)	77901	630-01-3	524 B				624 B
n-C28 (Appendix C)	78116	630-02-4	525 B				625 B
n-C30 (Appendix C)	78117	638-68-6	526 B		d62	93952-07-9	626 B
carbazole (4c)	77571	86-74-8	528 B		d8	38537-24-5	628 B
2-chloronaphthalene	34581	91-58-7	020 B	016 B	d7	93951-84-9	220 B
4-chlorophenyl phenyl ether	34641	7005-72-3	040 B	017 B	d5	93951-85-0	240 B
chrysene	34320	218-01-9	076 B	018 B	d12	1719-03-5	276 B
p-cymene (Appendix C)	77356	99-87-6	513 B		d14	93952-03-5	613 B
dibenzo(a,h)anthracene	34556	53-70-3	082 B	019 B	d14	13250-98-1	282 B
dibenzofuran (Appendix C & 4c)	81302	132-64-9	505 B		d8	93952-04-6	605 B
dibenzothiophene (Synfuel)	77639	132-65-0	504 B		d8	33262-29-2	604 B
di-n-butyl phthalate	39110	84-74-2	068 B	026 B	d4	93952-11-5	268 B
1,2-dichlorobenzene	34536	95-50-1	025 B	020 B	d4	2199-69-1	225 B
1,3-dichlorobenzene	34566	541-73-1	026 B	021 B	d4	2199-70-4	226 B
1,4-dichlorobenzene	34571	106-46-7	027 B	022 B	d4	3855-82-1	227 B
3,3'-dichlorobenzidine	34631	91-94-1	028 B	023 B	d6	93951-91-8	228 B
diethyl phthalate	34336	84-66-2	070 B	024 B	d4	93952-12-6	270 B
2,4-dimethylphenol	34606	105-67-9	034 A	003 A	d3	93951-75-8	234 A
dimethyl phthalate	34341	131-11-3	071 B	025 B	d4	93951-89-4	271 B
2,4-dinitrotoluene	34611	121-14-2	035 B	027 B	d3	93951-68-9	235 B
2,6-dinitrotoluene	34626	606-20-2	036 B	028 B	d3	93951-90-7	236 B
di-n-octyl phthalate	34596	117-84-0	069 B	029 B	d4	93952-13-7	269 B
diphenylamine (Appendix C)	77579	122-39-4	507 B		d10	37055-51-9	607 B
diphenyl ether (Appendix C)	77587	101-84-8	508 B		d10	93952-05-7	608 B
1,2-diphenylhydrazine	34346	122-66-7	037 B	030 B	d10	93951-92-9	237 B
fluoranthene	34376	206-44-0	039 B	031 B	d10	93951-69-0	231 B
fluorene	34381	86-73-7	080 B	032 B	d10	81103-79-9	080 B

hexachlorobenzene	39700	118-74-1	009 B	033 B	13C6	93952-14-8	209 B
hexachlorobutadiene	34391	87-68-3	052 B	034 B	13C4	93951-70-3	252 B
hexachloroethane	34396	67-72-1	012 B	036 B	13C	93952-15-9	212 B
hexachlorocyclopentadiene	34386	77-47-4	053 B	035 B	13C4	93951-71-4	253 B
ideno(1,2,3-cd)pyrene	34403	193-39-5	083 B	037 B			
isophorone	34408	78-59-1	054 B	038 B	d8	93952-16-0	254 B
naphthalene	34696	91-20-3	055 B	039 B	d8	1146-65-2	255 B
beta-naphthylamine (Appendix C)	82553	91-59-8	502 B		d7	93951-94-1	602 B
nitrobenzene	34447	98-95-3	056 B	040 B	d5	4165-60-0	256 B
N-nitrosodimethylamine	34438	62-75-9	061 B	041 B	d6	17829-05-9	261 B
N-nitrosodi-n-proplyamine	34428	621-64-7	063 B	042 B	d14	93951-96-3	263 B
N-nitrosodiphenylamine	34433	86-30-6	062 B	043 B	d6	93951-95-2	262 B
phenanthrene	34461	85-01-8	081 B	044 B	d10	1517-22-2	281 B
phenol	34694	108-95-2	065 A	010 A	d5	4165-62-2	265 A
alpha-picoline (Synfuel)	77088	109-06-8	503 B		d7	93951-93-0	503 B
pyrene	34469	129-00-0	084 B	045 B	d10	1718-52-1	284 B
styrene (Appendix C)	77128	100-42-5	510 B		d5	5161-29-5	610 B
alphe-terpineol (Appendix C)	77493	98-55-5	509 B		d3	93952-06-8	609 B
1,2,3-trichlorobenzene (4c)	77613	87-61-6	529 B		d3	3907-98-0	629 B
1,2,4-trichlorobenzene	34551	120-82-1	008 B	046 B	d3	93952-16-0	208 B

Table 2

Acid Extractable Compounds Determined by Calibrated GCMS Using Isotope Dilution and Internal Standard Techniques

		Pollutant			Labeled Compound		
Compound	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
4-chloro-3-methylphenol	34452	59-50-7	022 A	008 A	d2	93951-72-5	222 A
2-chlorophenol	34586	95-57-8	024 A	001 A	d4	93951-73-6	224 A
2,4-dichlorophenol	34601	120-83-2	031 A	002 A	d3	93951-74-7	231 A
2,4-dinitrophenol	34616	51-28-5	059 A	005 A	d3	93951-77-0	259 A
2-methyl-4,6-dinitrophenol	34657	534-52-1	060 A	004 A	d2	93951-76-9	260 A
2-nitrophenol	34591	88-75-5	057 A	006 A	d4	93951-75-1	257 A
4-nitrophenol	34646	100-02-7	058 A	007 A	d4	93951-79-2	258 A
pentachlorophenol	39032	87-86-5	064 A	009 A	13C6	85380-74-1	264 A
2,3,6-trichlorophenol (4c)	77688	933-75-5	530 A		d2	93951-81-6	630 A
2,4,5-trichlorophenol (4c)		95-95-4	531 A		d2	93951-82-7	631 A
2,4,6-trichlorophenol	34621	88-06-2	021 A	011 A	d2	93951-80-5	221 A

Table 3

Base/neutral Extractable Compounds to be Determined by Reverse Search and Quantitation using Known Retention Times, Response Factors, Reference Compound, and Mass Spectra

EGD No.	Compound	CAS Registry
555	acetophenone	98-86-2
556	4-aminobiphenyl	92-67-1
557	aniline	62-53-3
558	o-anisidine	90-04-0
559	aramite	140-57-9
560	benzanthrone	82-05-3
561	1,3-benzenediol (resorcinol)	108-46-3
562	benzenethiol	108-98-5
563	2,3-benzofluorene	243-17-4
564	benzyl alcohol	100-51-6
565	2-bromochlorobenzene	694-80-4
566	3-bromochlorobenzene	108-37-2
567	4-chloro-2-nitroaniline	89-63-4
568	5-chloro-o-toluidine	95-79-4
569	4-chloroaniline	106-47-8
570	3-chloronitrobenzene	121-73-3
571	o-cresol	95-48-7
572	crotoxyphos	7700-17-6
573	2,6-di-tert-butyl-p-benzoquinone	719-22-2
574	2,4-diaminotoluene	95-80-7
575	1,2-dibromo-3-chloropropane	96-12-8
576	2,6-dichloro-4-nitroaniline	99-30-9
577	1,3-dichloro-2-propanol	96-23-1
578	2,3-dichloroaniline	608-27-5
579	2,3-dichloronitrobenzene	3209-22-1
580	1,2:3,4-diepoxybutane	1464-53-5
581	3,3'-dimethoxybenzidine	119-90-4
582	dimethyl sulfone	67-71-0
583	p-dimethylaminoazobenzene	60-11-7
584	7,12-dimethylbenz(a)anthracene	57-97-6
585	N,N-dimethylformamide	68-12-2
586	3,6-dimethylphenanthrene	1576-67-6
587	1,3-dinitrobenzene	100-25-4
588	diphenyldisulfide	882-33-7
589	ethyl methanesulfonate	62-50-0
590	ethylenethiourea	96-45-7
591	ethynylestradiol 3-methyl ether	72-33-3
592	hexachloropropene	1888-71-7
593	2-isopropylnaphthalene	2027-17-0
594	isosafrole	120-58-1
595	longifolene	475-20-7
596	malachite green	569-64-2
597	methapyrilene	91-80-5
598	methyl methanesulfonate	66-27-3
599	2-methylbenzothioazole	120-75-2
900	3-methylcholanthrene	56-49-5
901	4,4'-methylenebis(2-chloroaniline)	101-14-4
902	4,5-methylenephenanthrene	203-64-5
903	1-methylfluorene	1730-37-6
904	2-methylnaphthalene	91-57-6

905	1-methylphenanthrene	832-69-9
906	2-(methylthio)benzothiazole	120-75-2
907	1,5-naphthalenediamine	2243-62-1
908	1,4-naphthoquinone	130-15-4
909	alpha-naphthylamine	134-32-7
910	5-nitro-o-toluidine	99-55-8
911	2-nitroaniline	88-77-4
912	3-nitroaniline	99-09-2
913	4-nitroaniline	100-01-6
914	4-nitrobiphenyl	92-93-3
915	N-nitrosodi-n-butylamine	924-16-3
916	N-nitrosodiethylamine	55-18-5
917	N-nitrosomethylethylamine	10595-95-6
918	N-nitrosomethylphenylamine	614-00-6
919	N-nitrosomorpholine	59-89-2
920	N-nitrosopiperidine	100-75-4
921	pentachlorobenzene	608-93-5
922	pentachloroethane	76-01-7
923	pentamethylbenzene	700-12-9
924	perylene	198-55-0
925	phenacetin	62-44-2
926	phenothiazine	92-84-2
927	1-phenylnaphthalene	605-02-7
928	2-phenylnaphthalene	612-94-2
929	pronamide	23950-58-5
930	pyridine	110-86-1
931	safrole	94-59-7
932	squalene	7683-64-9
933	1,2,4,5-tetrachlorobenzene	95-94-3
934	thianaphthene (2,3-benzothiophene)	95-15-8
935	thioacetamide	62-55-5
936	thioxanthone	492-22-8
937	o-toluidine	95-53-4
938	1,2,3-trimethoxybenzene	634-36-6
939	2,4,5-trimethylaniline	137-17-7
940	triphenylene	217-59-4
941	tripropyleneglycol methyl ether	20324-33-8
942	1,3,5-trithiane	291-21-4

Table 4

Acid Extractable Compounds to be Determined by Reverse Search and Quantitation using Known Retention Times, Response Factors, Reference Compound, and Mass Spectra

EGD No.	Compound	CAS Registry
943	benzoic acid	65-85-0
944	p-cresol	106-44-5
945	3,5-dibromo-4-hydroxybenzonitrile	1689-84-5
946	2,6-dichlorophenol	87-65-0
947	hexanoic acid	142-62-1
948	2,3,4,6-tetrachlorophenol	58-90-2

Table 5

Gas Chromatography of Base/neutral Extractable Compounds

EGD No. (1)	Compound	Retention time			Minimum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
164	2,2'-difluorobiphenyl (int std)	1163	164	1.000 - 1.000	10		
930	pyridine	378	164	0.325			
261	N-nitrosodimethylamine-d6 (5)	378	164	0.286 - 0.364	50		
361	N-nitrosodimethylamine (5)	385	261	1.006 - 1.028	50	16	27
585	N,N-dimethylformamide	407	164	0.350			
580	1,2:3,4-diepoxybutane	409	164	0.352			
603	alpha picoline-d7	417	164	0.326 - 0.393	50		
703	alpha picoline	426	603	1.006 - 1.028	50	25	87
917	N-nitrosomethylethylamine	451	164	0.338			
598	methyl methanesulfonate	511	164	0.439			
610	styrene-d5	546	164	0.450 - 0.488	10		
710	styrene	549	610	1.002 - 1.009	10	149*	17
916	N-nitrosodiethylamine	570	164	0.490			
577	1,3-dichloro-2-propanol	589	164	0.506			
589	ethyl methanesulfonate	637	164	0.548			
582	dimethyl sulfone	649	164	0.558			
562	benzenethiol	667	164	0.574			
922	pentachloroethane	680	164	0.585			
557	aniline	694	164	0.597			
613	p-cymene-d14	742	164	0.624 - 0.652	10		
713	p-cymene	755	613	1.008 - 1.023	10	426*	912*
265	phenol-d5	696	164	0.584 - 0.613	10		
365	phenol	700	265	0.995 - 1.010	10	2501*	757*
218	bis(2-chloroethyl) ether-d8	696	164	0.584 - 0.607	10		
318	bis(2-chloroethyl) ether	704	218	1.007 - 1.016	10	32	22
617	n-decane-d22	698	164	0.585 - 0.615	10		
717	n-decane	720	617	1.022 - 1.038	10	299*	1188*
226	1,3-dichlorobenzene-d4	722	164	0.605 - 0.636	10		
326	1,3-dichlorobenzene	724	226	0.998 - 1.008	10	46	26
227	1,4-dichlorobenzene-d4	737	164	0.601 - 0.666	10		
327	1,4-dichlorobenzene	740	227	0.997 - 1.009	10	35	20
225	1,2-dichlorobenzene-d4	758	164	0.632 - 0.667	10		
325	1,2-dichlorobenzene	760	225	0.995 - 1.008	10	63	16
935	thioacetamide	768	164	0.660			
564	benzyl alcohol	785	164	0.675			
242	bis(2-chloroisopropyl) ether-d12	788	164	0.664 - 0.691	10		
342	bis(2-chloroisopropyl) ether	799	262	1.010 - 1.016	10	24	39
571	o-cresol	814	164	0.700			
263	N-nitrosodi-n-propylamine-d14 (5)	817	164	0.689 - 0.716	20		
363	N-nitrosodi-n-propylamine (5)	830	263	1.008 - 1.023	20	46	47
555	acetophenone	818	164	0.703			
212	hexachloroethane-13C	819	164	0.690 - 0.717	10		
312	hexachloroethane	823	212	0.999 - 1.001	10	58	55
937	o-toluidine	830	164	0.714			
919	N-nitrosomorpholine	834	164	0.717			
575	1,2-dibromo-3-chloropropane	839	164	0.721			
256	nitrobenzene-d5	845	164	0.706 - 0.727	10		
356	nitrobenzene	849	256	1.002 - 1.007	10	39	28
566	3-bromochlorobenzene	854	164	0.734			

565	2-bromochlorobenzene	880	164	0.757			
941	tripropylene glycol methyl ether	881	164	0.758			
254	isophorone-d8	881	164	0.747 - 0.767	10		
354	isophorone	889	254	0.999 - 1.017	10	8	5
942	1,3,5-trithiane	889	164	0.764			
920	N-nitrosopiperidine	895	164	0.770			
234	2,4-dimethylphenol-d3	921	164	0.781 - 0.803	10		
334	2,4-dimethylphenol	924	234	0.999 - 1.003	10	26	13
243	bis(2-chloroethoxy) methane-d6 (5)	933	164	0.792 - 0.807	10		
343	bis(2-chloroethoxy) methane (5)	939	243	1.000 - 1.013	10	26	23
208	1,2,4-trichlorobenzene-d3	955	164	0.813 - 0.830	10		
308	1,2,4-trichlorobenzene	958	208	1.000 - 1.005	10	49	24
558	o-anisidine	962	164	0.827			
255	naphthalene-d8	963	164	0.819 - 0.836	10		
355	naphthalene	967	255	1.001 - 1.006	10	62	42
934	thianapthene	971	164	0.835			
609	alpha-terpineol-d3	973	164	0.829 - 0.844	10		
709	alpha-terpineol	975	609	0.998 - 1.008	10	nd	nd
606	n-dodecane-d26	953	164	0.730 - 0.908	10		
706	n-dodecane	981	606	0.986 - 1.051	10	860*	3885*
629	1,2,3-trichlorobenzene-d3 (5)	1000	164	0.852 - 0.868	10		
729	1,2,3-trichlorobenzene (5)	1003	629	1.000 - 1.005	10	260*	164*
252	hexachlorobutadiene-13C4	1005	164	0.856 - 0.871	10		
352	hexachlorobutadiene	1006	252	0.999 - 1.002	10	46	22
918	N-nitrosomethylphenylamine	1006	164	0.865			
592	hexachloropropene	1013	164	0.871			
569	4-chloroaniline	1016	164	0.874			
570	3-chloronitrobenzene	1018	164	0.875			
915	N-nitrosodi-n-butylamine	1063	164	0.914			
923	pentamethylbenzene	1083	164	0.931			
561	1,3-benzenediol	1088	164	0.936			
931	safrole	1090	164	0.937			
939	2,4,5-trimethylaniline	1091	164	0.938			
904	2-methylnaphthalene	1098	164	0.944			
599	2-methylbenzothiazole	1099	164	0.945			
568	5-chloro-o-toluidine	1101	164	0.947			
938	1,2,3-trimethoxybenzene	1128	164	0.970			
933	1,2,4,5-tetrachlorobenzene	1141	164	0.981			
253	hexachlorocyclopentadiene-13C4	1147	164	0.976 - 0.986	10		
353	hexachlorocyclopentadiene	1142	253	0.999 - 1.001	10	nd	nd
594	isosafrole (cis or trans)	1147	164	0.986			
594	isosafrole (cis or trans)	1190	164	1.023			
578	2,3-dichloroaniline	1160	164	0.997			
574	2,4-diaminotoluene	1187	164	1.021			
220	2-chloronaphthalene-d7	1185	164	1.014 - 1.024	10		
320	2-chloronaphthalene	1200	220	0.997 - 1.007	10	80	59
518	n-tetradecane	1203	164	1.034	10	256	3533
612	biphenyl-d10	1195	164	1.016 - 1.027	10		
712	biphenyl	1205	612	1.001 - 1.006	10	67	55
608	diphenyl ether-d10	1211	164	1.036 - 1.047	10		
708	diphenyl ether	1216	608	0.997 - 1.009	10	44	12
579	2,3-dichloronitrobenzene	1214	164	1.044			
911	2-nitroaniline	1218	164	1.047			
908	1,4-naphthoquinone	1224	164	1.052			
595	longifolene	1225	164	1.053			
277	acenaphthylene-d8	1265	164	1.080 - 1.095	10		
377	acenaphthylene	1247	277	1.000 - 1.004	10	57	18
593	2-isopropylnaphthalene	1254	164	1.078			

587	1,3-dinitrobenzene	1255	164	1.079			
576	2,6-dichloro-4-nitroaniline	1259	164	1.083			
271	dimethyl phthalate-d4	1269	164	1.083 - 1.102	10		
371	dimethyl phthalate	1273	271	0.998 - 1.005	10	62	21
573	2,6-di-t-butyl-p-benzoquinone	1273	164	1.095			
236	2,6-dinitrotoluene-d3	1283	164	1.090 - 1.112	10		
336	2,6-dinitrotoluene	1300	236	1.001 - 1.005	10	55	47
912	3-nitroaniline	1297	164	1.115			
201	acenaphthene-d10	1298	164	1.107 - 1.125	10		
301	acenaphthene	1304	201	0.999 - 1.009	10	64	55
605	dibenzofuran-d8	1331	164	1.134 - 1.155	10		
705	dibenzofuran	1335	605	0.998 - 1.007	10	77	210*
921	pentachlorobenzene	1340	164	1.152			
909	alpha-naphthylamine	1358	164	1.168			
235	2,4-dinitrotoluene-d3	1359	164	1.152 - 1.181	10		
335	2,4-dinitrotoluene	1364	235	1.000 - 1.002	10	65	209*
602	beta-naphthylamine-d7	1368	164	1.163 - 1.189	50		
702	beta-naphthylamine	1371	602	0.996 - 1.007	50	49	37
590	ethylenethiourea	1381	164	1.187			
280	fluorene-d10	1395	164	1.185 - 1.214	10		
380	fluorene	1401	281	0.999 - 1.008	10	69	61
240	4-chlorophenyl phenyl ether-d5	1406	164	1.194 - 1.223	10		
340	4-chlorophenyl phenyl ether	1409	240	0.990 - 1.015	10	73	59
270	diethyl phthalate-d4	1409	164	1.197 - 1.229	10		
370	diethyl phthalate	1414	270	0.996 - 1.006	10	52	16
906	2-(methylthio)benzothiazole	1415	164	1.217			
567	4-chloro-2-nitroaniline	1421	164	1.222			
910	5-nitro-o-toluidine	1422	164	1.223			
913	4-nitroaniline	1430	164	1.230			
619	n-hexadecane-d34	1447	164	1.010 - 1.478	10		
719	n-hexadecane	1469	619	1.013 - 1.020	10	116*	644*
237	1,2-diphenylhydrazine-d8	1433	164	1.216 - 1.248	20		
337	1,2-diphenylhydrazine (6)	1439	237	0.999 - 1.009	20	48	27
607	diphenylamine-d10	1437	164	1.213 - 1.249	20		
707	diphenylamine	1439	607	1.000 - 1.007	20	58	54
262	N-nitrosodiphenylamine-d6	1447	164	1.225 - 1.252	20		
362	N-nitrosodiphenylamine (7)	1464	262	1.000 - 1.002	20	55	36
241	4-bromophenyl phenyl ether-d5 (5)	1495	164	1.271 - 1.307	10		
341	4-bromophenyl phenyl ether (5)	1498	241	0.990 - 1.015	10	55	17
925	phenacetin	1512	164	1.300			
903	1-methylfluorene	1514	164	1.302			
209	hexachlorobenzene-13C6	1521	164	1.288 - 1.327	10		
309	hexachlorobenzene	1522	209	0.999 - 1.001	10	51	48
556	4-aminobiphenyl	1551	164	1.334			
929	pronamide	1578	164	1.357			
281	phenanthrene-d10	1578	164	1.334 - 1.380	10		
520	n-octadecane	1580	164	1.359	10	134*	344*
381	phenanthrene	1583	281	1.000 - 1.005	10	42	22
278	anthracene-d10	1588	164	1.342 - 1.388	10		
378	anthracene	1592	278	0.998 - 1.006	10	52	21
604	dibenzothiophene-d8	1559	164	1.314 - 1.361	10		
704	dibenzothiophene	1564	604	1.000 - 1.006	10	72	71
588	diphenyldisulfide	1623	164	1.396			
914	4-nitrobiphenyl	1639	164	1.409			
927	1-phenylnaphthalene	1643	164	1.413			
628	carbazole-d8 (5)	1645	164	1.388 - 1.439	20		
728	carbazole (5)	1650	628	1.000 - 1.006	20	47	24
621	n-eicosane-d42	1655	164	1.184 - 1.662	10		

721	n-eicosane	1677	621	1.010 - 1.021	10	83	229*
907	1,5-naphthalenediamine	1676	164	1.441			
902	4,5-methylenephenanthrene	1690	164	1.453			
905	1-methylphenanthrene	1697	164	1.459			
268	di-n-butyl phthalate-d4	1719	164	1.446 - 1.510	10		
368	di-n-butyl phthalate	1723	268	1.000 - 1.003	10	64	80
928	2-phenylnaphthalene	1733	164	1.490			
586	3,6-dimethylphenanthrene	1763	164	1.516			
597	methapyrilene	1781	164	1.531			
926	phenothiazine	1796	164	1.544			
239	fluoranthene-d10	1813	164	1.522 - 1.596	10		
339	fluoranthene	1817	239	1.000 - 1.004	10	54	22
572	crotoxyphos	1822	164	1.567			
936	thioxanthone	1836	164	1.579			
284	pyrene-d10	1844	164	1.523 - 1.644	10		
384	pyrene	1852	284	1.001 - 1.003	10	40	48
205	benzidine-d8	1854	164	1.549 - 1.632	50		
305	benzidine	1853	205	1.000 - 1.002	50	nd	nd
522	n-docosane	1889	164	1.624	10	432*	447*
559	aramite	1901	164	1.635			
559	aramite	1916	164	1.647			
583	p-dimethylaminoazobenzene	1922	164	1.653			
563	2,3-benzofluorene	1932	164	1.661			
623	n-tetracosane-d50	1997	164	1.671 - 1.764	10		
723	n-tetracosane	2025	612	1.012 - 1.015	10	--	--
932	squalene	2039	164	1.753			
267	butylbenzyl phthalate-d4 (5)	2058	164	1.715 - 1.824	10		
367	butylbenzyl phthalate (5)	2060	267	1.000 - 1.002	10	60	65
276	chrysene-d12	2081	164	1.743 - 1.837	10		
376	chrysene	2083	276	1.000 - 1.004	10	51	48
901	4,4'methylenebis(2-chloroaniline)	2083	164	1.791			
272	benzo(a)anthracene-d12	2082	164	1.735 - 1.846	10		
372	benzo(a)anthracene	2090	272	0.999 - 1.007	10	61	47
581	3,3'-dimethoxybenzidine	2090	164	1.797			
228	3,3'-dichlorobenzidine-d6	2088	164	1.744 - 1.848	50		
328	3,3'-dichlorobenzidine	2086	228	1.000 - 1.001	50	62	111
940	triphenylene	2088	164	1.795			
560	benzanthrone	2106	164	1.811			
266	bis(2-ethylhexyl) phthalate-d4	2123	164	1.771 - 1.880	10		
366	bis(2-ethylhexyl) phthalate	2124	266	1.000 - 1.002	10	553*	1310*
524	n-hexacosane	2147	164	1.846	10	609*	886*
591	ethynylestradiol 3-methyl ether	2209	164	1.899			
269	di-n-octyl phthalate-d4	2239	164	1.867 - 1.982	10		
369	di-n-octyl phthalate	2240	269	1.000 - 1.002	10	72	62
525	n-octacosane	2272	164	1.954	10	492*	1810*
584	7,12-dimethylbenz(a)anthracene	2284	164	1.964			
274	benzo(b)fluoranthene-d12	2281	164	1.902 - 2.025	10		
374	benzo(b)fluoranthene	2293	274	1.000 - 1.005	10	54	30
275	benzo(k)fluoranthene-d12	2287	164	1.906 - 2.033	10		
375	benzo(k)fluoranthene	2293	275	1.000 - 1.005	10	95	20
924	perylene	2349	164	2.020			
273	benzo(a)pyrene-d12	2351	164	1.954 - 2.088	10		
373	benzo(a)pyrene	2350	273	1.000 - 1.004	10	52	15
626	n-triacontane-d62	2384	164	1.972 - 2.127	10		
726	n-triacontane	2429	626	1.011 - 1.028	10	252*	658*
596	malachite green	2382	164	2.048			
900	3-methylcholanthrene	2439	164	2.097			
083	indeno(1,2,3-cd)pyrene	2650	164	2.279	20	67	263*

282	dibenzo(a,h)anthracene-d14 (5)	2649	164	2.107 - 2.445	20		
382	dibenzo(a,h)anthracene (5)	2660	282	1.000 - 1.007	20	49	125
279	benzo(ghi)perylene-d12	2741	164	2.187 - 2.524	20		
379	benzo(ghi)perylene	2750	279	1.001 - 1.006	20	44	nd

(1) Reference numbers beginning with 0, 1, 5, or 9 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.
(2) Single values in this column are based on single laboratory data.
(3) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points. The concentration in the aqueous or solid phase is determined using the equations in section 14.
(4) Method detection limits determined in digested sludge (low solids) and in filter cake or compost (high solids).
(5) Specification derived from related compound.
(6) Detected as azobenzene
(7) Detected as diphenylamine
nd = not detected when spiked into the sludge tested
*Background levels of these compounds were present in the sludge tested, resulting in higher than expected MDL's. The MDL for these compounds is expected to be approximately 50 ug/kg with no interferences present.

Column: 30 +/- 2 m x 0.25 +/- 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary
Temperature program: 5 min at 30 ^{o}C; 30 - 280 ^{o}C at 8 ^{o}C per min; isothermal at 280 ^{o}C until benzo(ghi)perylene elutes
Gas velocity: 30 +/- 5 cm/sec at 30 ^{o}C

Table 6

Gas Chromatography of Acid Extractable Compounds

EGD No. (1)	Compound	Retention time			Minimum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
164	2,2'-difluorobiphenyl (int std)	1163	164	1.000 - 1.000	10		
224	2-chlorophenol-d4	701	164	0.587 - 0.618	10		
324	2-chlorophenol	705	224	0.997 - 1.010	10	18	10
947	hexanoic acid	746	164	0.641			
944	p-cresol	834	164	0.717			
257	2-nitrophenol-d4	898	164	0.761 - 0.783	20		
357	2-nitrophenol	900	257	0.994 - 1.009	20	39	44
231	2,4-dichlorophenol-d3	944	164	0.802 - 0.822	10		
331	2,4-dichlorophenol	947	231	0.997 - 1.006	10	24	116
943	benzoic acid	971	164	0.835			
946	2,6-dichlorophenol	981	164	0.844			
222	4-chloro-3-methylphenol-d2	1086	164	0.930 - 0.943	10		
322	4-chloro-3-methylphenol	1091	222	0.998 - 1.003	10	41	62
221	2,4,6-trichlorophenol-d2	1162	164	0.994 - 1.005	10	46	111
321	2,4,6-trichlorophenol	1165	221	0.998 - 1.004	10		
631	2,4,5-trichlorophenol-d2 (5)	1167	164	0.998 - 1.009	10		
731	2,4,5-trichlorophenol	1170	631	0.998 - 1.004	10	32	55
530	2,3,6-trichlorophenol	1195	164	1.028	10	58	37
259	2,4-dinitrophenol-d3	1323	164	1.127 - 1.149	50		
359	2,4-dinitrophenol	1325	259	1.000 - 1.005	50	565	642
258	4-nitrophenol-d4	1349	164	1.147 - 1.175	50		
358	4-nitrophenol	1354	258	0.997 - 1.006	50	287	11
948	2,3,4,6-tetrachlorophenol	1371	164	1.179			
260	2-methyl-4,6-dinitrophenol-d2	1433	164	1.216 - 1.249	20		
360	2-methyl-4,6-dinitrophenol	1435	260	1.000 - 1.002	20	385	83
945	3,5-dibromo-4-hydroxybenzonitrile	1481	164	1.273			
264	pentachlorophenol-13C6	1559	164	1.320 - 1.363	50		
364	pentachlorophenol	1561	264	0.998 - 1.002	50	51	207

(1) Reference numbers beginning with 0, 1, 5, or 9 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.
(2) Single values in this column are based on single laboratory data
(3) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points. The concentration in the aqueous or solid phase is determined using the equations in section 14.
(4) Method detection limits determined in digested sludge (low solids) and in filter cake or compost (high solids).
*Background levels of these compounds were present in the sludge resulting in higher than expected MDL's. The MDL for these compounds is expected to be approximately 50 ug/kg with no interferences present.
(5) Specification derived from related compound.

Column: 30 +/- 2 m x 0.25 +/- 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary
Temperature program: 5 min at 30 °C; 30 - 250 °C or until pentachlorophenol elutes

Gas velocity: 30 +/- 5 cm/sec at 30 °C

Table 7

DFTPP Mass-intensity Specifications*

Mass	Intensity required
51	8 - 82 percent of m/z 198
68	less than 2 percent of m/z 69
69	11 - 91 percent of m/z 198
70	less than 2 percent of m/z 69
127	32 - 59 percent of m/z 198
197	less than 1 percent of m/z 198
198	base peak, 100 percent abundance
199	4 - 9 percent of m/z 198
275	11 - 30 percent of m/z 198
441	44 - 110 percent of m/z 442
442	30 - 86 percent of m/z 198
443	14 - 24 percent of m/z 442

*Reference 6

Table 8

Base/neutral Extractable Compound Characteristic m/z's and Response Factors

Compound	Labeled analog	Primary m/z	Response Factor (1)
acenaphthene	d10	154/164	
acenaphthylene	d8	152/160	
acetophenone		105	0.79
4-aminobiphenyl		169	0.81
aniline		93	1.04
o-anisidine		108	0.43
anthracene	d10	178/188	
aramite		185	0.19
benzanthrone		230	0.15
1,3-benzenediol		110	0.78
benzenethiol		110	0.18
benzidine	d8	184/192	
benzo(a)anthracene	d12	228/240	
benzo(b)fluoranthene	d12	252/264	
benzo(k)fluoranthene	d12	252/264	
benzo(a)pyrene	d12	252/264	
benzo(ghi)perylene	d12	276/288	
2,3-benzofluorene		216	0.35
benzoic acid		105	0.16
benzyl alcohol		79	0.47
biphenyl	d10	154/164	
bis(2-chloroethyl) ether	d8	93/101	
bis(2-chloroethoxy)methane	d8	93/97	
bis(2-chloroisopropyl) ether	d12	121/131	
bis(2-ethylhexyl) phthalate	d4	149/153	
2-bromochlorobenzene		111	0.33
3-bromochlorobenzene		192	0.40
4-bromophenyl phenyl ether	d5	248/255	
butyl benzyl phthalate	d4	149/153	
n-C10	d22	55/66	
n-C12	d26	55/66	
n-C14		55	
n-C16	d34	55/66	
n-C18		55	
n-C20	d42	55/66	
n-C22		55	
n-C24	d50	55/66	
n-C26		55	
n-C28		55	
n-C30	d62	55/66	
carbazole	d8	167/175	
4-chloro-2-nitroaniline		172	0.20
5-chloro-o-toluidine		106	0.50
4-chloroaniline		127	0.73
2-chloronaphthalene	d7	162/169	
3-chloronitrobenzene		157	0.18
4-chlorophenyl phenyl ether	d5	204/209	
3-chloropropionitrile		54	0.42
chrysene	d12	228/240	
o-cresol		108	0.59
crotoxyphos		127	0.017

p-cymene	d14	119/130	
2,6-di-tert-butyl-p-benzoquinone		220	0.078
di-n-butyl phthalate	d4	149/153	
2,4-diaminotoluene		122	0.059
dibenzo(a,h)anthracene	d14	278/292	
dibenzofuran	d8	168/176	
dibenzothiophene	d8	184/192	
1,2-dibromo-3-chloropropane		157	0.22
2,6-dichloro-4-nitroaniline		124	0.019
1,3-dichloro-2-propanol		79	0.68
2,3-dichloroaniline		161	0.47
1,2-dichlorobenzene	d4	146/152	
1,3-dichlorobenzene	d4	146/152	
1,4-dichlorobenzene	d4	146/152	
3,3'-dichlorobenzidine	d6	252/258	
2,2'-difluorobiphenyl (int std)		190	
2,3-dichloronitrobenzene		191	0.11
1,2:3,4-diepoxybutane		55	0.27
diethyl phthalate	d4	149/153	
3,3'-dimethoxybenzidine		244	0.19
dimethyl phthalate	d4	163/167	
dimethyl sulfone		79	0.40
p-dimethylaminoazobenzene		120	0.23
7,12-dimethylbenz(a)anthracene		256	0.58
N,N-dimethylformamide		73	0.51
3,6-dimethylphenanthrene		206	0.72
2,4-dimethylphenol	d3	122/125	
1,3-dinitrobenzene		168	0.24
2,4-dinitrotoluene	d3	165/168	
2,6-dinitrotoluene	d3	165/167	
di-n-octyl phthalate	d4	149/153	
diphenylamine	d10	169/179	
diphenyl ether	d10	170/180	
diphenyldisulfide		218	0.25
1,2-diphenylhydrazine (2)	d10	77/82	
ethyl methanesulfonate		109	0.28
ethylenethiourea		102	0.22
ethynylestradiol 3-methyl ether		227	0.28
fluoranthene	d10	202/212	
fluorene	d10	166/176	
hexachlorobenzene	$^{13}C_6$	284/292	
hexachlorobutadiene	$^{13}C_4$	225/231	
hexachloroethane	^{13}C	201/204	
hexachlorocyclopentadiene	$^{13}C_4$	237/241	
hexachloropropene		213	0.23
indeno(1,2,3-cd)pyrene		276	
isophorone	d8	82/88	
2-isopropylnaphthalene		170	0.32
isosafrole		162	0.33
longifolene		161	0.14
malachite green		330	
methapyrilene		97	0.43
methyl methanesulfonate		80	0.20
2-methylbenzothiazole		149	0.59
3-methylcholanthrene		268	0.59
4,4'-methylenebis(2-chloroaniline)		231	0.21
4,5-methylenephenanthrene		190	0.44
1-methylfluorene		180	0.37

2-methylnaphthalene		142	0.99
1-methylphenanthrene		192	0.65
2-(methylthio)benzothiazole		181	0.42
naphthalene	d8	128/136	
1,5-naphthalenediamine		158	0.085
1,4-naphthoquinone		158	0.021
alpha-naphthylamine		143	0.89
beta-naphthylamine	d7	143/150	
5-nitro-o-toluidine		152	0.31
2-nitroaniline		138	0.39
3-nitroaniline		138	0.27
4-nitroaniline		138	0.11
nitrobenzene	d5	128/128	
4-nitrobiphenyl		199	0.35
N-nitrosodi-n-butylamine		84	0.47
N-nitrosodi-n-propylamine	d14	70/78	
N-nitrosodiethylamine		102	0.45
N-nitrosodimethylamine	d6	74/80	
N-nitrosodiphenylamine (3)	d6	169/175	
N-nitrosomethylethylamine		88	0.33
N-nitrosomethylphenylamine		106	0.024
N-nitrosomorpholine		56	0.49
N-nitrosopiperidine		114	0.41
pentachlorobenzene		248	0.25
pentachloroethane		117	0.20
pentamethylbenzene		148	0.42
perylene		252	0.30
phenacetin		108	0.38
phenanthrene	d10	178/188	
phenol	d5	94/71	
phenothiazine		199	0.15
1-phenylnaphthalene		204	0.48
2-phenylnaphthalene		204	0.73
alpha-picoline	d7	93/100	
pronamide		173	0.31
pyrene	d10	202/212	
pyridine		79	0.68
safrole		162	0.45
squalene		69	0.042
styrene	d5	104/109	
alpha-terpineol	d3	59/62	
1,2,4,5-tetrachlorobenzene		216	0.43
thianaphthene		134	1.52
thioacetamide		75	0.28
thioxanthone		212	0.23
o-toluidine		106	1.04
1,2,3-trichlorobenzene	d3	180/183	
1,2,4-trichlorobenzene	d3	180/183	
1,2,3-trimethoxybenzene		168	0.48
2,4,5-trimethylaniline		120	0.28
triphenylene		228	1.32
tripropylene glycol methyl ether		59	0.092
1,3,5-trithiane		138	0.15

(1) referenced to 2,2'-difluorobiphenyl
(2) detected as azobenzene
(3) detected as diphenylamine

Table 9

Acid Extractable Compound Characteristic m/z's

Compound	Labeled analog	Primary m/z	Response Factor (1)
benzoic acid		105	0.16
4-chloro-3-methylphenol	d2	107/109	
2-chlorophenol	d4	128/132	
p-cresol		108	0.61
3,5-dibromo-4-hydroxybenzonitrile		277	0.12
2,4-dichlorophenol	d3	162/167	
2,6-dichlorophenol		162	0.42
2,4-dinitrophenol	d3	184/187	
hexanoic acid		60	0.62
2-methyl-4,6-dinitrophenol	d2	198/200	
2-nitrophenol	d4	139/143	
4-nitrophenol	d4	139/143	
pentachlorophenol	$^{13}C_6$	266/272	
2,3,4,6-tetrachlorophenol		232	0.17
2,3,6-trichlorophenol	d2	196/200	
2,4,5-trichlorophenol	d2	196/200	
2,4,6-trichlorophenol	d2	196/200	

(1) referenced to 2,2'-difluorobiphenyl

Table 10

Acceptance Criteria for Performance Tests

EGD No. (1)	Compound	Acceptance criteria				
		Initial precision and accuracy Section 8.2.3 (ug/L)		labeled compound recovery Sec 8.3 and 14.2	calibration verification Sec 12.5	On-going accuracy Sec 12.7
		s	X	P (%)	(ug/mL)	R (ug/L)
301	acenaphthene	21	79 - 134		80 - 125	72 - 144
201	acenaphthene-d10	38	38 - 147	20 - 270	71 - 141	30 - 180
377	acenaphthylene	38	69 - 186		60 - 166	61 - 207
277	acenaphthylene-d8	31	39 - 146	23 - 239	66 - 152	33 - 168
378	anthracene	41	58 - 174		60 - 168	50 - 199
278	anthracene-d10	49	31 - 194	14 - 419	58 - 171	23 - 242
305	benzidine	119	16 - 518		34 - 296	11 - 672
205	benzidine-d8	269	ns(2) ns	ns - ns	ns - ns	ns - ns
372	benzo(a)anthracene	20	65 - 168		70 - 142	62 - 176
272	benzo(a)anthracene-d12	41	25 - 298	12 - 605	28 - 357	22 - 329
374	benzo(b)fluoranthene	183	32 - 545		61 - 164	20 - ns
274	benzo(b)fluoranthene-d12	168	11 - 577	ns - ns	14 - ns	ns - ns
375	benzo(k)fluoranthene	26	59 - 143		13 - ns	53 - 155
275	benzo(k)fluoranthene-d12	114	15 - 514	ns - ns	13 - ns	ns - 685
373	benzo(a)pyrene	26	62 - 195		78 - 129	59 - 206
273	benzo(a)pyrene-d12	24	35 - 181	21 - 290	12 - ns	32 - 194
379	benzo(ghi)perylene	21	72 - 160		69 - 145	58 - 168
279	benzo(ghi)perylene-d12	45	29 - 268	14 - 529	13 - ns	25 - 303
712	biphenyl (Appendix C)	41	75 - 148		58 - 171	62 - 176
612	biphenyl-d10	43	28 - 165	ns - ns	52 - 192	17 - 267
318	bis(2-chloroethyl) ether	34	55 - 196		61 - 164	50 - 213
218	bis(2-chloroethyl) ether-d8	33	29 - 196	15 - 372	52 - 194	25 - 222
343	bis(2-chloroethoxy)methane	27	43 - 153		44 - 228	39 - 166
243	bis(2-chloroethoxy)methane-d8(3)	33	29 - 196	15 - 372	52 - 194	25 - 222
342	bis(2-chloroisopropyl) ether	17	81 - 138		67 - 148	77 - 145
242	bis(2-chloroisopropyl)ether-d12	27	35 - 149	20 - 260	44 - 229	30 - 169
366	bis(2-ethylhexyl) phthalate	31	69 - 220		76 - 131	64 - 232
266	bis(2-ethylhexyl) phthalate-d4	29	32 - 205	18 - 364	43 - 232	28 - 224
341	4-bromophenyl phenyl ether	44	44 - 140		52 - 193	35 - 172
241	4-bromophenylphenyl ether-d5(3)	52	40 - 161	19 - 325	57 - 175	29 - 212
367	butyl benzyl phthalate	31	19 - 233		22 - 450	35 - 170
267	butyl benzyl phthalate-d4 (3)	29	32 - 205	18 - 364	43 - 232	28 - 224
717	n-C10 (Appendix C)	51	24 - 195		42 - 235	19 - 237
617	n-C10-d22	70	ns - 298	ns - ns	44 - 227	ns - 504
706	n-C12 (Appendix C)	74	35 - 369		60 - 166	29 - 424
606	n-C12-d26	53	ns - 331	ns - ns	41 - 242	ns - 408
518	n-C14 (Appendix C) (3)	109	ns - ns		37 - 268	ns - ns
719	n-C16 (Appendix C)	33	80 - 162		72 - 138	71 - 181
619	n-C16-d34	46	37 - 162	18 - 308	54 - 186	28 - 202
520	n-C18 (Appendix C) (3)	39	42 - 131		40 - 249	35 - 167
721	n-C20 (Appendix C)	59	53 - 263		54 - 184	46 - 301
621	n-C20-d42	34	34 - 172	19 - 306	62 - 162	29 - 198
522	n-C22 (Appendix C) (3)	31	45 - 152		40 - 249	39 - 195
723	n-C24 (Appendix C)	11	80 - 139		65 - 154	78 - 142
623	n-C24-d50	28	27 - 211	15 - 376	50 - 199	25 - 229
524	n-C26 (Appendix C) (3)	35	35 - 193		26 - 392	31 - 212
525	n-C28 (Appendix C) (3)	35	35 - 193		26 - 392	31 - 212

726	n-C30 (Appendix C)	32	61 - 200		66 - 152	56 - 215
626	n-C30-d62	41	27 - 242	13 - 479	24 - 423	23 - 274
728	carbazole (4c)	38	36 - 165		44 - 227	31 - 188
628	carbazole-d8 (3)	31	48 - 130	29 - 215	69 - 145	40 - 156
320	2-chloronaphthalene	100	46 - 357		58 - 171	35 - 442
220	2-chloronaphthalene-d7	41	30 - 168	15 - 324	72 - 139	24 - 204
322	4-chloro-3-methylphenol	37	76 - 131		85 - 115	62 - 159
222	4-chloro-3-methylphenol-d2	111	30 - 174	ns - 613	68 - 147	14 - 314
324	2-chlorophenol	13	79 - 135		78 - 129	76 - 138
224	2-chlorophenol-d4	24	36 - 162	23 - 255	55 - 180	33 - 176
340	4-chlorophenyl phenyl ether	42	75 - 166		71 - 142	63 - 194
240	4-chlorophenyl phenyl ether-d5	52	40 - 161	19 - 325	57 - 175	29 - 212
376	chrysene	51	59 - 186		70 - 142	48 - 221
276	chrysene-d12	69	33 - 219	13 - 512	24 - 411	23 - 290
713	p-cymene (Appendix C)	18	76 - 140		79 - 127	72 - 147
613	p-cymene-d14	67	ns - 359	ns - ns	66 - 152	ns - 468
382	dibenzo(a,h)anthracene	55	23 - 299		13 - 761	19 - 340
282	dibenzo(a,h)anthracene-d14 (3)	45	29 - 268	14 - 529	13 - ns	25 - 303
705	dibenzofuran (Appendix C)	20	85 - 136		73 - 136	79 - 146
605	dibenzofuran-d8	31	47 - 136	28 - 220	66 - 150	39 - 160
704	dibenzothiophene (Synfuel)	31	79 - 150		72 - 140	70 - 168
604	dibenzothiophene-d8	31	48 - 130	29 - 215	69 - 145	40 - 156
368	di-n-butyl phthalate	15	76 - 165		71 - 142	74 - 169
268	di-n-butyl phthalate-d4	23	23 - 195	13 - 346	52 - 192	22 - 209
325	1,2-dichlorobenzene	17	73 - 146		74 - 135	70 - 152
225	1,2-dichlorobenzene-d4	35	14 - 212	ns - 494	61 - 164	11 - 247
326	1,3-dichlorobenzene	43	63 - 201		65 - 154	55 - 225
226	1,3-dichlorobenzene-d4	48	13 - 203	ns - 550	52 - 192	ns - 260
327	1,4-dichlorobenzene	42	61 - 194		62 - 161	53 - 219
227	1,4-dichlorobenzene-d4	48	15 - 193	ns - 474	65 - 153	11 - 245
328	3,3'-dichlorobenzidine	26	68 - 174		77 - 130	64 - 185
228	3,3'-dichlorobenzidine-d6	80	ns - 562	ns - ns	18 - 558	ns - ns
331	2,4-dichlorophenol	12	85 - 131		67 - 149	83 - 135
231	2,4-dichlorophenol-d3	28	38 - 164	24 - 260	64 - 157	34 - 182
370	diethyl phthalate	44	75 - 196		74 - 135	65 - 222
270	diethyl phthalate-d4	78	ns - 260	ns - ns	47 - 211	ns - ns
334	2,4-dimethylphenol	13	62 - 153		67 - 150	60 - 156
234	2,4-dimethylphenol-d3	22	15 - 228	ns - 449	58 - 172	14 - 242
371	dimethyl phthalate	36	74 - 188		73 - 137	67 - 207
271	dimethyl phthalate-d4	108	ns - 640	ns - ns	50 - 201	ns - ns
359	2,4-dinitrophenol	18	72 - 134		75 - 133	68 - 141
259	2,4-dinitrophenol-d3	66	22 - 308	ns - ns	39 - 256	17 - 378
335	2,4-dinitrotoluene	18	75 - 158		79 - 127	72 - 164
235	2,4-dinitrotoluene-d3	37	22 - 245	10 - 514	53 - 187	19 - 275
336	2,6-dinitrotoluene	30	80 - 141		55 - 183	70 - 159
236	2,6-dinitrotoluene-d3	59	44 - 184	17 - 442	36 - 278	31 - 250
369	di-n-octyl phthalate	16	77 - 161		71 - 140	74 - 166
269	di-n-octyl phthalate-d4	46	12 - 383	ns - ns	21 - 467	10 - 433
707	diphenylamine (Appendix C)	45	58 - 205		57 - 176	51 - 231
607	diphenylamine-d10	42	27 - 206	11 - 488	59 - 169	21 - 249
708	diphenyl ether (Appendix C)	19	82 - 136		83 - 120	77 - 144
608	diphenyl ether-d10	37	36 - 155	19 - 281	77 - 129	29 - 186
337	1,2-diphenylhydrazine	73	49 - 308		75 - 134	40 - 360
237	1,2-diphenylhydrazine-d10	35	31 - 173	17 - 316	58 - 174	26 - 200
339	fluoranthene	33	71 - 177		67 - 149	64 - 194
239	fluoranthene-d10	35	36 - 161	20 - 278	47 - 215	30 - 187
380	fluorene	29	81 - 132		74 - 135	70 - 151
280	fluorene-d10	43	51 - 131	27 - 238	61 - 164	38 - 172

309	hexachlorobenzene	16	90 - 124		78 - 128	85 - 132
209	hexachlorobenzene-13C6	81	36 - 228	13 - 595	38 - 265	23 - 321
352	hexachlorobutadiene	56	51 - 251		74 - 135	43 - 287
252	hexachlorobutadiene-13C4	63	ns - 316	ns - ns	68 - 148	ns - 413
312	hexachloroethane	227	21 - ns		71 - 141	13 - ns
212	hexachloroethane-13C1	77	ns - 400	ns - ns	47 - 212	ns - 563
353	hexachlorocyclopentadiene	15	69 - 144		77 - 129	67 - 148
253	hexachlorocyclopentadiene-13C4	60	ns - ns	ns - ns	47 - 211	ns - ns
083	ideno(1,2,3-cd)pyrene (3)	55	23 - 299		13 - 761	19 - 340
354	isophorone	25	76 - 156		70 - 142	70 - 168
254	isophorone-d8	23	49 - 133	33 - 193	52 - 194	44 - 147
360	2-methyl-4,6-dinitrophenol	19	77 - 133		69 - 145	72 - 142
260	2-methyl-4,6-dinitrophenol-d2	64	36 - 247	16 - 527	56 - 177	28 - 307
355	naphthalene	20	80 - 139		73 - 137	75 - 149
255	naphthalene-d8	39	28 - 157	14 - 305	71 - 141	22 - 192
702	beta-naphthylamine (Appendix C)	49	10 - ns		39 - 256	ns - ns
602	beta-naphthylamine-d7	33	ns - ns	ns - ns	44 - 230	ns - ns
356	nitrobenzene	25	69 - 161		85 - 115	65 - 169
256	nitrobenzene-d5	28	18 - 265	ns - ns	46 - 219	15 - 314
357	2-nitrophenol	15	78 - 140		77 - 129	75 - 145
257	2-nitrophenol-d4	23	41 - 145	27 - 217	61 - 163	37 - 158
358	4-nitrophenol	42	62 - 146		55 - 183	51 - 175
258	4-nitrophenol-d4	188	14 - 398	ns - ns	35 - 287	ns - ns
361	N-nitrosodimethylamine	49	10 - ns		39 - 256	ns - ns
261	N-nitrosodimethylamine-d6 (3)	33	ns - ns	ns - ns	44 - 230	ns - ns
363	N-nitrosodi-n-propylamine	45	65 - 142		68 - 148	53 - 173
263	N-nitrosodi-n-propylamine (3)	37	54 - 126	26 - 256	59 - 170	40 - 166
362	N-nitrosodiphenylamine	45	65 - 142		68 - 148	53 - 173
262	N-nitrosodiphenylamine-d6	37	54 - 126	26 - 256	59 - 170	40 - 166
364	pentachlorophenol	21	76 - 140		77 - 130	71 - 150
264	pentachlorophenol-13C6	49	37 - 212	18 - 412	42 - 237	29 - 254
381	phenanthrene	13	93 - 119		75 - 133	87 - 126
281	phenanthrene-d10	40	45 - 130	24 - 241	67 - 149	34 - 168
365	phenol	36	77 - 127		65 - 155	62 - 154
265	phenol-d5	161	21 - 210	ns - ns	48 - 208	ns - ns
703	alpha-picoline (Synfuel)	38	59 - 149		60 - 165	50 - 174
603	alpha-picoline-d7	138	11 - 380	ns - ns	31 - 324	ns - 608
384	pyrene	19	76 - 152		76 - 132	72 - 159
284	pyrene-d10	29	32 - 176	18 - 303	48 - 210	28 - 196
710	styrene (Appendix C)	42	53 - 221		65 - 153	48 - 244
610	styrene-d5	49	ns - 281	ns - ns	44 - 228	ns - 348
709	alpha-terpineol (Appendix C)	44	42 - 234		54 - 186	38 - 258
609	alpha-terpineol-d3	48	22 - 292	ns - 672	20 - 502	18 - 339
729	1,2,3-trichlorobenzene (4c)	69	15 - 229		60 - 167	11 - 297
629	1,2,3-trichlorobenzene-d3 (3)	57	15 - 212	ns - 592	61 - 163	10 - 282
308	1,2,4-trichlorobenzene	19	82 - 136		78 - 128	77 - 144
208	1,2,4-trichlorobenzene-d3	57	15 - 212	ns - 592	61 - 163	10 - 282
530	2,3,6-trichlorophenol (4c) (3)	30	58 - 137		56 - 180	51 - 153
731	2,4,5-trichlorophenol (4c)	30	58 - 137		56 - 180	51 - 153
631	2,4,5-trichlorophenol-d2 (3)	47	43 - 183	21 - 363	69 - 144	34 - 226
321	2,4,6-trichlorophenol	57	59 - 205		81 - 123	48 - 244
221	2,4,6-trichlorophenol-d2	47	43 - 183	21 - 363	69 - 144	34 - 226

(1) Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

(2) ns = no specification: limit is outside the range that can be measured reliably.

(3) This compound is to be determined by internal standard; specification is derived from related compound.

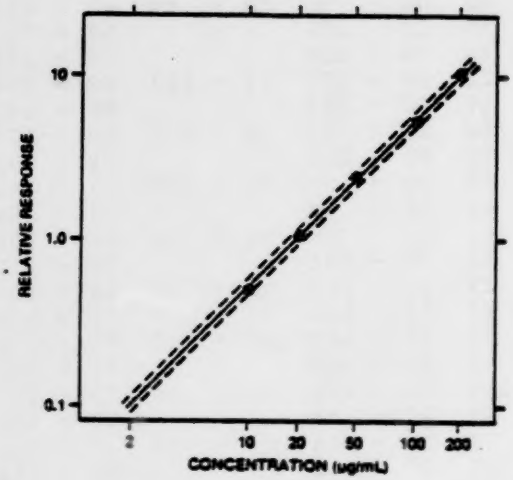

FIGURE 1 Relative Response Calibration Curve for Phenol. The Dotted Lines Enclose a ± 10 Percent Error Window.

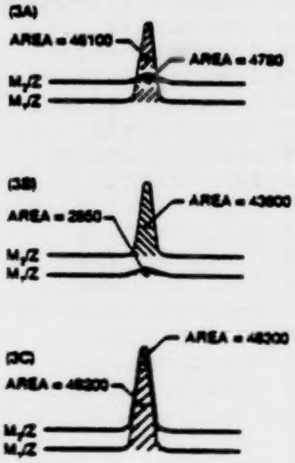
(3A)
AREA = 46100
AREA = 4780
M_2/Z
M_1/Z
(3B)
AREA = 2650
AREA = 43600
M_2/Z
M_1/Z
(3C)
AREA = 48300
AREA = 48200
M_2/Z
M_1/Z

FIGURE 3 Extracted Ion Current Profiles for (3A) Unlabeled Compound, (3B) Labeled Compound, and (3C) Equal Mixture of Unlabeled and Labeled Compounds.

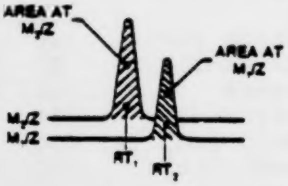
AREA AT M_2/Z
AREA AT M_1/Z
M_2/Z
M_1/Z
RT_1
RT_2

FIGURE 2 Extracted Ion Current Profiles for Chromatographically Resolved Labeled (m_2/z) and Unlabeled (m_1/z) Pairs.

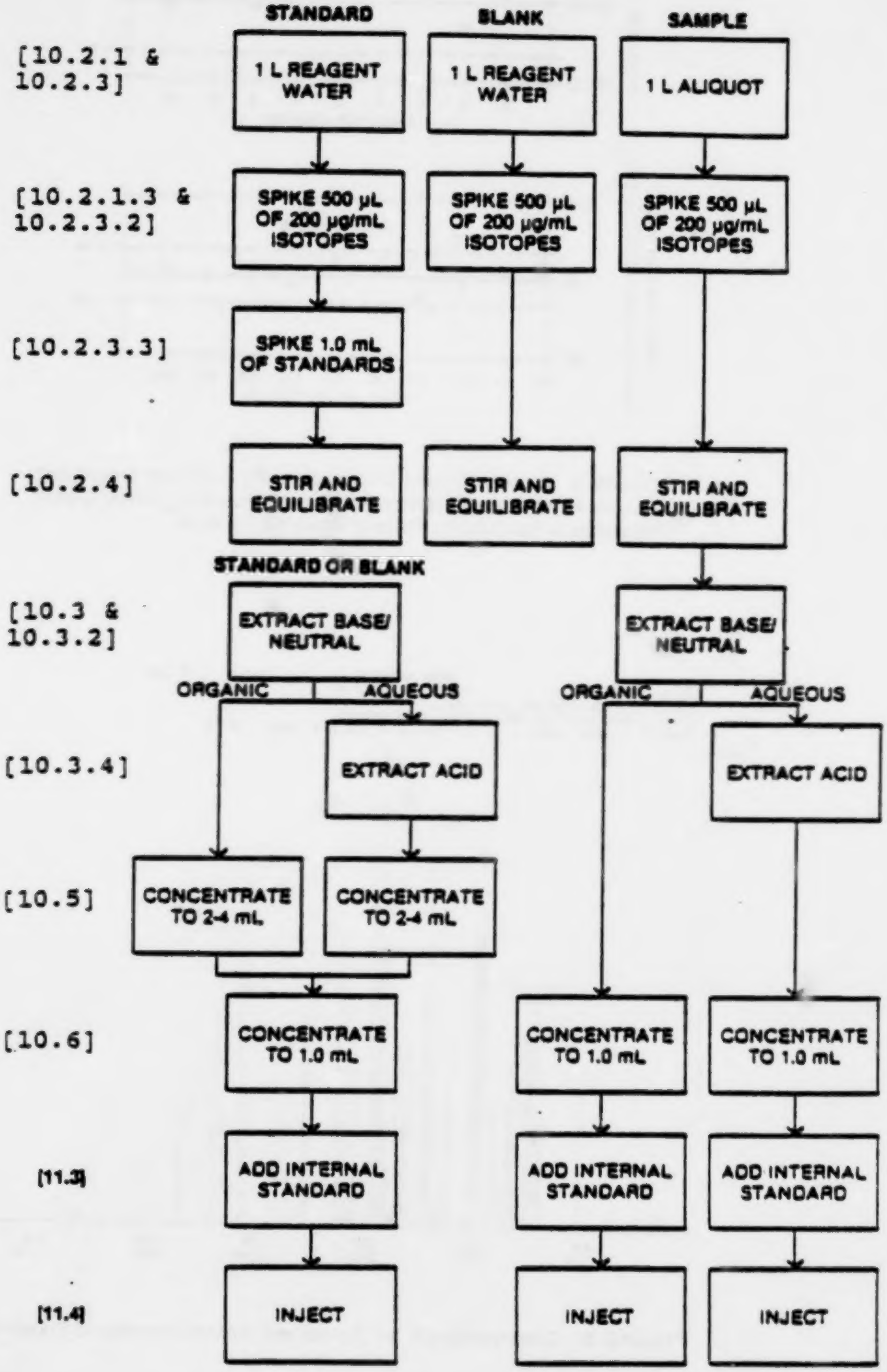
STANDARD
BLANK
SAMPLE
[10.2.1 & 10.2.3]
1 L REAGENT WATER
1 L REAGENT WATER
1 L ALIQUOT
[10.2.1.3 & 10.2.3.2]
SPIKE 500 µL OF 200 µg/mL ISOTOPES
SPIKE 500 µL OF 200 µg/mL ISOTOPES
SPIKE 500 µL OF 200 µg/mL ISOTOPES
[10.2.3.3]
SPIKE 1.0 mL OF STANDARDS
[10.2.4]
STIR AND EQUILIBRATE
STIR AND EQUILIBRATE
STIR AND EQUILIBRATE
STANDARD OR BLANK
[10.3 & 10.3.2]
EXTRACT BASE/ NEUTRAL
EXTRACT BASE/ NEUTRAL
ORGANIC
AQUEOUS
ORGANIC
AQUEOUS
[10.3.4]
EXTRACT ACID
EXTRACT ACID
[10.5]
CONCENTRATE TO 2-4 mL
CONCENTRATE TO 2-4 mL
[10.6]
CONCENTRATE TO 1.0 mL
CONCENTRATE TO 1.0 mL
CONCENTRATE TO 1.0 mL
[11.3]
ADD INTERNAL STANDARD
ADD INTERNAL STANDARD
ADD INTERNAL STANDARD
[11.4]
INJECT
INJECT
INJECT

FIGURE 4 Flow Chart for Extraction/Concentration of Precision and Recovery Standard, Blank, and Sample by Method 1625. Numbers in Brackets [ ] Refer to Section Numbers in the Method.

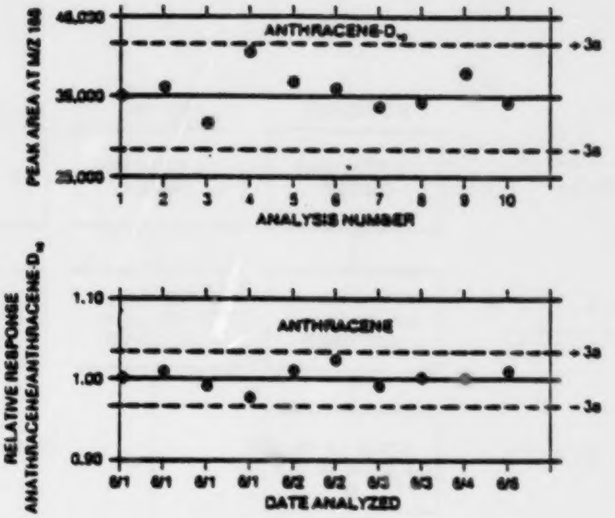

FIGURE 5 Quality Control Charts Showing Area (top graph) and Relative Response of Anthracene to Anthracene-d_{10} (lower graph) Plotted as a Function of Time or Analysis Number.

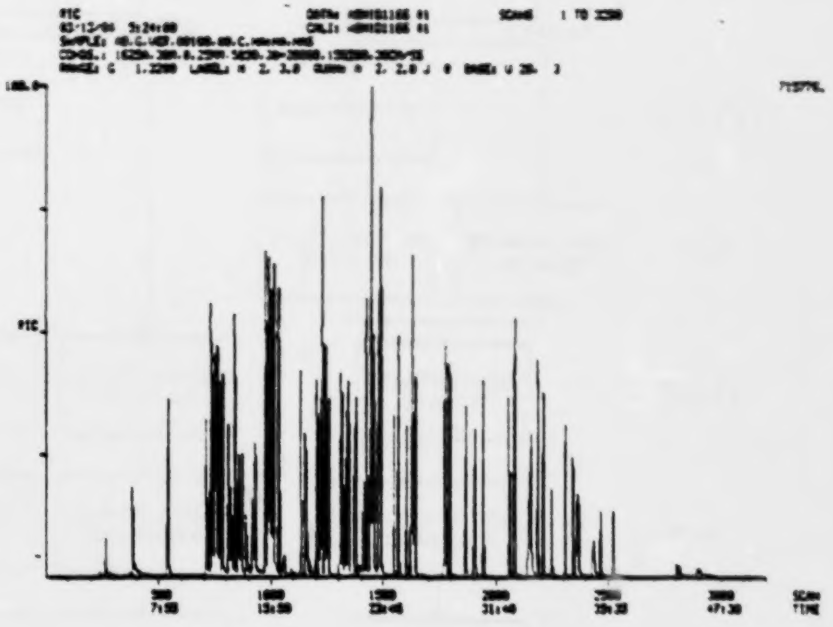

FIGURE 6 Chromatogram of Combined Acid/base/neutral Standard.

Appendix A: Mass Spectra in the Form of Mass/Intensity Lists

555 acetophenone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	21	43	245	49	19	50	221	51	524	52	75
61	13	62	26	63	422	65	31	73	13	74	64
75	36	76	62	77	941	78	11	89	12	91	22
105	1000	106	87	120	479	121	38				

556 4-aminobiphenyl

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	55	63	65	72	82	83	73	85	163	115	142
139	65	141	132	167	163	168	280	169	1000	170	216

557 aniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	65	41	66	42	16	46	11	47	75	50	40
51	47	52	54	53	12	54	40	61	17	62	28
63	59	64	33	65	226	66	461	74	11	78	14
91	10	92	136	93	1000	94	73				

558 o-anisidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	22	41	43	42	10	50	60	51	106	52	202
53	286	54	39	61	12	62	25	63	43	64	24
65	142	66	20	76	13	77	36	68	32	79	25
80	915	81	41	92	47	93	14	94	18	105	18
108	1000	109	55	122	123	844	124	56			

559 aramite

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	606	57	758	59	328	63	782	65	285	74	113
77	155	91	339	105	153	107	239	121	107	123	120
163	143	175	182	185	1000	187	328	191	346	197	191
319	270	334	137								

560 benzanthrone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	69	75	71	87	97	88	160	99	69	100	215
101	278	150	58	174	67	199	63	200	350	201	236
202	762	203	126	230	1000	231	177				

561 1,3-benzenediol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	64	41	19	52	42	43	36	49	11	50	43
51	54	52	29	53	184	54	89	55	97	61	15
62	27	63	74	64	61	65	13	68	56	69	119
71	16	81	201	82	251	95	13	109	11	110	1000
111	51										

562 benzenethiol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	128	50	149	51	205	65	175	66	505	69	114
77	161	84	259	109	316	110	1000	111	102		

563 2,3-benzofluorene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	52	81	69	94	143	95	253	106	60	107	205
108	491	187	75	189	90	213	233	214	60	215	987
216	1000	217	166								

943 benzoic acid

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	29	50	221	51	413	52	45	66	11	74	53
75	25	76	81	77	778	78	76	105	1000	122	868

564 benzyl alcohol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	17	59	16	50	155	51	319	52	78	53	84
61	11	62	31	63	70	64	12	65	75	74	35
75	13	76	18	77	565	78	116	79	1000	80	73
89	65	90	64	91	125	105	38	106	18	107	523
108	737	109	43								

565 2-bromochlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	237	50	890	51	183	73	158	74	506	75	1000
76	202	111	961	113	287	190	638	192	809	194	193

566 3-bromochlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	201	50	834	51	174	73	169	74	509	75	914
76	197	111	1000	113	301	190	625	192	802	194	191

567 4-chloro-2-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	119	50	174	51	260	52	531	61	205	62	394
63	1000	64	315	65	192	73	290	74	105	75	156
76	127	78	152	90	724	91	253	101	232	114	312
126	766	128	234	142	211	172	915	174	289		

568 5-chloro-o-toluidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	115	51	261	52	257	53	137	77	420	78	134
79	140	89	152	106	1000	140	599	141	964	142	265
143	313										

569 4-chloroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	60	62	55	63	147	64	135	65	329	73	51
91	63	92	186	99	67	100	115	127	1000	128	81
129	292										

570 3-chloronitrobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	619	51	189	73	144	74	330	75	1000	76	169
85	101	99	258	111	851	113	266	157	424	159	137

571 o-cresol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	102	51	181	53	144	77	358	79	380	80	159
89	114	90	231	107	783	108	1000				

944 p-cresol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	136	51	224	52	106	53	196	77	420	79	308
80	145	90	122	107	822	108	1000				

572 crotoxyphos

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	633	44	448	67	42	77	70	79	41	104	100
105	484	109	21	127	1000	166	180	193	401	194	20

573 2,6-di-t-butyl-p-benzoquinone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	392	53	586	55	325	57	668	65	416	67	927
77	376	79	308	91	456	95	322	107	248	121	255
135	538	136	240	149	429	163	292	177	1000	205	203
220	410										

574 2,4-diaminotoluene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	70	42	55	51	76	52	70	53	51	61	91
67	50	77	147	78	69	93	63	94	224	104	128
105	134	106	67	121	958	122	1000	123	79		

575 1,2-dibromo-3-chloropropane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	38	59	341	51	104	61	38	75	1000	76	75
77	331	81	43	93	117	95	106	97	12	105	67
106	17	119	74	121	66	155	635	157	784	158	20
159	204	187	10								

945 3,5-dibromo-4-hydroxybenzonitrile

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
53	148	61	193	62	222	88	632	117	137	168	152
170	141	275	489	277	1000	279	451				

576 2,6-dichloro-4-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	206	52	1000	61	523	62	828	63	588	73	470
65	137	89	218	90	443	97	458	124	954	126	401
133	218	160	401	176	431	178	134	206	378		

577 1,3-dichloro-2-propanol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	14	42	55	43	503	44	22	47	12	58	15
49	113	50	15	51	37	57	10	61	12	75	14
78	11	79	1000	80	25	81	310				

578 2,3-dichloroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
52	138	61	151	62	265	63	455	64	142	65	105
73	130	90	460	99	202	125	108	126	149	161	1000
163	626	165	101								

579 2,3-dichloronitrobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	220	50	257	61	150	62	120	63	173	73	336
74	976	75	743	84	351	85	166	86	125	109	1000
110	204	111	303	133	701	135	435	145	580	147	368
161	190	163	121	191	411	193	263				

946 2,6-dichlorophenol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	111	62	160	63	714	73	132	98	293	99	117
126	260	162	1000	164	613	166	101				

580 1,2:3,4-diepoxybutane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	37	41	29	42	83	43	60	55	1000	56	67
57	155	58	16	85	13						

581 3,3'-dimethoxybenzidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
65	44	79	222	85	69	93	84	107	46	115	110
122	115	158	154	186	144	201	552	229	162	244	1000
245	152										

582 dimethyl sulfone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	10	45	94	46	29	47	18	48	69	62	14
63	69	64	22	65	19	79	1000	81	36	94	528
96	23										

583 p-dimethylaminoazobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	483	51	181	77	447	78	120	79	147	91	109
104	142	105	190	120	1000	148	160	225	676		

584 7,12-dimethylbenzo(a)anthracene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
101	24	112	34	113	112	114	38	119	212	120	296
125	46	126	81	127	60	128	76	215	24	226	47
237	23	239	313	240	230	241	433	242	61	250	32
252	68	253	33	255	84	256	1000	257	180		

585 N,N-dimethylformamide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	58	41	79	42	497	43	115	44	1000	45	19
57	17	58	83	72	89	73	994	74	35		

586 3,6-dimethylphenanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
76	113	89	129	94	179	101	142	102	151	189	388
190	193	191	430	205	246	206	1000	207	159		

587 1,3-dinitrobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	1000	51	131	63	228	64	218	74	311	75	623
76	664	92	240	122	166	168	399				

588 diphenyldisulfide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	153	51	293	65	671	59	282	77	141	109	1000
110	132	154	191	185	117	218	418				

589 ethyl methanesulfonate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	16	43	72	45	208	48	40	59	19	63	23
64	22	65	93	79	1000	80	127	81	42	96	16
97	206	109	579	111	18	123	15	124	33		

590 ethylenethiourea

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	46	42	126	45	97	46	42	59	14	72	89
73	151	102	1000								

591 ethynylestradiol 3-methyl ether

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	155	53	101	91	157	115	143	147	226	159	132
160	115	173	199	174	313	227	1000	228	149	242	153
310	516										

592 hexachloropropene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	131	71	333	106	334	108	200	117	329	119	320
141	206	143	196	211	631	213	1000	215	623	217	186

947 hexanoic acid

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	627	42	535	43	214	45	186	46	19	55	128
56	90	57	102	60	1000	61	66	69	21	70	20
73	412	74	56	87	98						

593 2-isopropylnaphthalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	100	63	111	76	157	77	129	115	147	127	131
128	216	152	133	153	184	154	114	155	1000	156	139
170	368										

594 isosafrole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	110	51	222	63	127	77	277	78	208	103	355
104	441	131	371	132	107	135	129	161	250	162	1000

595 longifolene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
53	438	55	719	65	346	67	453	77	566	69	713
91	1000	93	611	94	546	95	404	105	614	107	475
119	394	133	338	161	568	204	172				

596 malachite green

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
118	113	126	313	165	369	208	135	209	233	210	181
237	158	253	1000	254	160	329	189	330	775	331	170

597 methapyriline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	72	45	47	53	40	58	1000	71	188	72	225
78	54	79	48	97	516	190	40	191	67		

598 methyl methanesulfonate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	178	56	15	48	108	50	26	63	35	64	48
65	285	78	27	79	821	80	1000	81	44	82	33
95	137	109	59	110	60						

599 2-methylbenzothiozole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	152	50	133	58	153	62	106	63	309	69	513
82	204	108	392	109	102	148	279	149	1000	150	110

900 3-methylcholanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
113	58	119	55	125	83	126	305	132	99	133	122
134	160	250	56	252	322	253	271	263	59	265	106
266	50	267	192	268	1000	269	185				

901 4,4'-methylenebis(2-chloroaniline)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
77	190	84	107	98	299	104	133	115	226	140	316
195	352	229	228	231	1000	233	227	265	171	266	631
267	144	268	358								

902 4,5-methylenephenanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	50	62	55	63	95	74	69	81	145	86	53
87	60	94	255	95	659	163	80	187	213	188	137
189	900	190	1000								

903 1-methylfluorene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	66	51	87	62	57	63	137	74	64	75	85
76	196	83	135	87	53	88	78	89	203	90	58
139	54	151	73	152	124	163	57	164	58	165	1000
166	136	176	96	177	52	178	202	179	182	180	686
181	99										

904 2-methylnaphthalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	29	51	39	57	28	58	47	62	26	63	65
65	19	69	56	70	25	71	126	74	25	75	23
76	14	77	15	86	13	87	18	89	42	113	19
114	13	115	303	116	25	126	13	139	98	140	24
141	748	142	1000	143	105						

905 1-methylphenanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	54	63	86	70	62	74	51	81	52	83	164
96	132	163	55	165	217	189	165	191	532	192	1000
193	152										

906 2-(methylthio)benzothiazole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	790	50	212	63	383	69	578	82	233	108	627
136	239	148	938	180	250	181	1000				

907 1,5-naphthalenediamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	48	65	83	77	75	79	111	103	86	118	52
130	262	131	40	141	43	157	89	158	1000	159	117

908 1,4-naphthoquinone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	445	51	62	52	52	66	69	74	189	75	205
76	590	101	51	102	613	103	52	104	550	130	433
158	1000	159	100								

909 alpha-naphthylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	25	51	31	57	36	59	46	62	28	63	59
65	27	71	58	72	104	89	62	113	22	114	34
115	401	116	212	142	53	143	1000	144	101		

910 5-nitro-o-toluidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	194	52	159	53	121	77	766	78	176	79	619
94	168	104	120	106	691	152	1000				

911 2-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	64	50	51	51	89	52	207	53	74	62	58
63	181	64	155	65	960	66	96	80	212	91	86
92	566	108	170	138	1000	139	63				

912 3-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	101	52	120	53	59	62	58	63	143	64	121
65	1000	66	114	80	169	91	62	92	764	93	62
108	87	138	717	139	51						

913 4-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
52	228	53	160	62	110	63	216	64	164	65	1000
66	124	80	266	92	300	108	636	138	520		

914 4-nitrobiphenyl

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	131	63	104	76	179	115	134	141	277	151	259
152	902	153	284	169	374	199	1000	200	125		

915 N-nitroso-di-n-butylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	1000	42	536	43	570	44	313	55	129	56	167
57	994	84	985	86	103	99	197	115	158	116	237
158	161										

916 N-nitrosodiethylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	170	42	079	43	69	44	1000	45	20	54	18
56	525	57	492	70	24	71	28	85	25	87	31
102	807	103	35								

917 N-nitrosomethylethylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	117	42	1000	43	667	44	26	54	17	56	189
57	99	59	13	71	60	73	57	88	772	89	20

918 N-nitrosomethylphenylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	181	51	434	52	104	63	110	77	1000	78	194
79	331	104	147	106	673	107	220	212	137		

919 N-nitrosomorpholine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	181	42	192	43	52	44	17	54	85	55	95
56	1000	57	49	85	13	86	333	87	14	116	337

920 N-nitrosopiperidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	320	42	1000	43	43	51	14	52	12	53	32
54	58	55	444	56	224	57	17	67	21	82	26
83	28	84	47	114	491	115	26				

921 pentachlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
73	160	108	239	125	102	178	102	213	179	215	218
217	106	248	648	250	1000	252	642	254	199		

922 pentachloroethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	203	60	398	62	119	83	378	85	218	94	114
95	165	117	1000	119	979	121	306	130	293	132	272
165	716	167	901	169	422						

923 pentamethylbenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	126	53	84	63	61	65	99	77	145	79	64
91	218	105	128	115	120	117	91	133	1000	134	105
147	60	148	420								

924 perylene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	33	111	43	112	70	113	111	124	132	125	251
126	243	224	49	248	75	249	52	250	284	251	86
252	1000	253	219								

925 phenacetin

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
43	443	51	33	52	112	53	164	63	39	64	30
65	47	79	31	80	179	31	154	108	1000	109	196
110	50	137	461	138	40	179	672	180	64		

926 phenothiazine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	145	51	120	63	134	69	190	100	128	154	149
166	240	167	607	198	186	199	1000	200	143		

927 1-phenylnaphthalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	132	51	156	63	148	74	124	75	142	76	136
87	101	88	183	89	162	100	155	101	527	102	111
200	144	201	136	202	643	203	1000	204	999	205	159

928 2-phenylnaphthalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	108	63	101	76	136	88	133	89	158	101	333
102	188	202	398	203	270	204	1000	205	157		

929 pronamide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	270	66	109	74	112	75	137	84	194	109	186
145	334	147	198	173	1000	175	615	254	133	255	211
256	102	257	122								

930 pyridine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	45	48	11	49	62	50	324	51	414	52	879
53	112	54	12	55	16	75	21	76	19	77	22
78	151	79	1000	80	101	81	58				

931 safrole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	132	51	369	63	108	77	391	78	228	103	348
104	477	105	130	131	437	132	166	161	298	162	1000
163	109										

932 squalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
53	62	55	94	67	105	68	119	69	1000	70	57
79	43	81	465	82	52	93	70	95	104	107	43
109	47	121	46	137	41						

933 1,2,4,5-tetrachlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	125	49	176	61	127	72	183	73	332	74	448
84	197	108	284	109	231	143	194	145	117	179	237
181	224	214	791	216	1000	218	482	220	101		

948 2,3,4,6-tetrachlorophenol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
61	234	65	167	66	105	83	134	84	178	96	202
97	107	131	463	133	270	166	298	168	273	194	168
196	164	230	793	232	1000	234	471				

934 thianaphthene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	80	50	91	51	65	62	82	63	162	67	78
69	139	74	55	89	191	90	136	108	82	134	1000
135	104	136	52								

935 thioacetamide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	225	42	485	43	44	46	18	57	36	58	93
59	165	60	437	75	1000	76	25	77	43		

936 thioxanthone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	262	63	180	69	320	74	116	69	176	82	121
92	188	108	129	139	385	152	227	183	112	184	951
185	137	212	1000	213	145						

937 o-toluidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	51	41	38	42	35	49	10	50	88	51	169
52	164	53	192	53	86	62	26	63	68	64	30
65	59	66	24	74	19	65	14	76	21	77	313
78	113	79	243	80	80	89	107	90	76	91	52
104	45	106	1000	107	90						

938 1,2,3-trimethoxybenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	257	51	459	52	139	53	276	63	112	65	341
67	114	77	246	79	132	82	117	93	483	95	801
107	190	108	144	110	898	125	578	153	759	168	1000

939 2,4,5-trimethylaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	80	52	58	51	63	53	66	65	150	67	74
79	62	91	167	93	51	117	54	118	65	119	93
120	1000	121	87	134	670	135	978	136	99		

940 triphenylene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	52	87	55	100	107	101	108	112	131	113	244
114	181	200	67	202	56	224	84	225	56	226	313
227	132	228	1000	229	184						

941 tripropylene glycol methyl ether

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	492	46	15	47	19	55	17	57	68	58	43
59	1000	60	34	71	16	72	44	73	363	74	232
103	57	117	92	161	21						

942 1,3,5-trithiane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
46	1000	47	150	48	98	59	93	60	76	64	136
73	102	91	92	92	111	110	58	138	259		

EPA METHOD
NO. 613M

United States Testing Company, Inc.
Metals and Environmental Chemistry Division

1415 PARK AVENUE
HOBOKEN, NEW JERSEY 07030 (201) 792-2400 (212) 943-0488

instrumental chemistry
trace analysis
analytical chemistry
methods development
chemical specialties
quality control
failure analysis

ON SHORE

August 22, 1986

AUG 25 1986

Sample Control Center
300 North Lee Street
Alexandria, VA 22314

Attention: Jim King

Reference: Episodes 1055, 1082, and 1084

Jim,

Enclosed please find the results of analysis for 2,3,7,8-TCDD and Total Tetra, Penta, Hexa and Hepta Dioxins and Furans for the above referenced episodes which include samples 15045, 15097, and 15099.

The following masses were used for identification and quantitation:

Compounds or Class	Masses
Total Tetra Dioxin	320,322
Total Tetra Furan	304,306
Total Penta Dioxin	354,356
Total Penta Furan	338,340
Total Hexa Dioxin	390,392
Total Hexa Furan	374,376
Total Hepta Dioxin	424,426
Total Hepta Furan	408,410
* Total Octa Dioxin	458,460
2,3,7,8-TCDD	320, 322, 257
2,3,7,8-TCDD Internal Std.	332, 334
2,3,7,8-TCDD Surrogate	328
OCDD Internal std.	472

* Octa Dioxins and Furans are no longer required but we have included this data for your information.

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A Member of the SGS Group (Societe Generale de Surveillance)

A sample was considered positive for a given isomer class only if both of the characteristic ions were present within two scans of each other.

Detection limits were calculated using the following formula:

$$DL = \frac{(M_1 + M_2) \times IS \times 2.5}{(M_3 + M_4) \times RF \times V}$$

M_1 = Peak Height of Noise for First Characteristic Mass of Analyte
M_2 = Peak Height of Noise for Second Characteristic Mass of Analyte
IS = ng Internal Standard
M_3 = Peak Height of First Characteristic Mass of Internal Standard
M_4 = Peak Height of Second Characteristic Mass of Internal Standard
RF = Response Factor
V = Volume of Sample Extracted (liters)

The response factor for TCDD was taken from the initial calibration of the instrument used for the analyses. Response factors for TCDF, PCDD, PCDF, HxCDD and HxCDF were calculated by analyzing a mixed standard of one isomer from each class and determining the ratio of the response of the analyte to the response of 1,2,3,4-TCDD. This ratio was then applied to the known response factor of 2,3,7,8-TCDD (it was assumed that 2,3,7,8-TDCC and 1,2,3,4-TCDD have the same response) relative to the internal standard, and a response factor of each analyte relative to the internal standard was determined.

Response factors for HpCDD, HpCDF and OCDD were determined by analysis of a mixed standard containing each of the analytes and OCDD internal standard.

All samples were subjected to the carbopak/celite clean-up described in the CLP TCDD procedure.

If you have any questions feel free to call.

Sincerely,

UNITED STATES TESTING CO., INC.

Jane M. Dunn
Manager
Environmental Chemistry

JMD/sm

Method 613—2,3,7,8-Tetrachlorodibenzo-p-Dioxin

1. Scope and Application

1.1 This method covers the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). The following parameter may be determined by this method:

Parameter	STORET No.	CAS No.
2,3,7,8-TCDD	34675	1746-01-6

1.2 This is a gas chromatographic/mass spectrometer (GC/MS) method applicable to the determination of 2,3,7,8-TCDD in municipal and industrial discharges as provided under 40 CFR 136.1. Method 625 may be used to screen samples for 2,3,7,8-TCDD. When the screening test is positive, the final qualitative confirmation and quantification miust be made using Method 613.

1.3 The method detection limit (MDL, defined in Section 14.1)[1] for 2,3,7,8-TCDD is listed in Table 1. The MDL for a specific wastewater may be different from that listed, depending upon the nature of interferences in the sample matrix.

1.4 Because of the extreme toxicity of this compound, the analyst must prevent exposure to himself, of to others, by materials knows or believed to contain 2,3,7,8-TCDD. Section 4 of this method contains guidelines and protocols that serve as minimum safe-handling standards in a limited-access laboratory.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is spiked with an internal standard of labeled 2,3,7,8-TCDD and extracted with methylene chloride using a separatory funnel. The methylene chloride extract is exchanged to hexane during concentration to a volume of 1.0 mL or less. The extract is then analysed by capillary column GC/MS to separate and measure 2,3,7,8-TCDD.[2-3]

2.2 The method provides selected column chromatographic cleanup proceudres to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the masses (m/z) monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.[4] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by the treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to mininmize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. 2,3,7,8-TCDD is often associated with other interfering chlorinated compounds which are at concentrations several magnitudes higher than that of 2,3,7,8-TCDD. The cleanup producers in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches [1,5-7] to eliminate false positives and achieve the MDL listed in Table 1.

3.3 The primary column, SP-2330 or equivalent, resolves 2,3,7,8-TCDD from the other 21 TCDD insomers. Positive results using any other gas chromatographic column must be confirmed using the primary column.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [8-10] for the information of the analyst. Benzene and 2,3,7,8-TCDD have been identified as suspected human or mammalian carcinogens.

4.2 Each laboratory must develop a strict safety program for handling 2,3,7,8-TCDD. The following laboratory practices are recommended:

4.2.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.

4.2.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the GC/MS should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

4.2.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength greater than 290 nm for several days. (Use F 40 BL lamps or equivalent). Analyze liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected.

4.3 Dow Chemical U.S.A. has issued the following precautions (revised November 1978) for safe handling of 2,3,7,8-TCDD in the laboratory:

4.3.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Inquiries about specific operations or uses may be addressed to the Dow Chemical Company. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. 2,3,7,8-TCDD is extremely toxic to laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

4.3.1.1 Protective equipment—Throw-away plastic gloves, apron or lab coat, safety glasses, and a lab hood adequate for radioactive work.

4.3.1.2 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

4.3.1.3 Personal hygiene—Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

4.3.1.4 Confinement—Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

4.3.1.5 Waste—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors must be trained in the safe handling of waste.

4.3.1.6 Disposal of wastes—2,3,7,8-TCDD decomposes above 800 °C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in a good incinerator. Gross quantities (milligrams) should be packaged securely and disposed through commercial or governmental channels which are capable of handling high-level radioactive wastes or extremely toxic wastes. Liquids should be allowed to evaporate in a good hood and in a disposable container. Residues may then be handled as above.

4.3.1.7 Decontamination—For personal decontamination, use any mild soap with plenty of scrubbing action. For decontamination of glassware, tools, and surfaces, Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. Dishwater may be disposed to the sewer. It is prudent to minimize solvent wastes because they may require special disposal through commercial sources which are expensive.

4.3.1.8 Laundry—Clothing known to be contaminated should be disposed with the precautions described under Section 4.3.1.6. Lab coats or other clothing worn in 2,3,7,8-TCDD work areas may be laundered.

Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing.

4.3.1.9 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by gas chromatography can achieve a limit of sensitivity of 0.1 µg per wipe. Less than 1 µg of 2,3,7,8-TCDD per sample indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe sample constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space. A high (>10 µg) 2,3,7,8-TCDD level indicates that unacceptable work practices have been employed in the past.

4.3.1.10 Inhalation—Any procedure that may produce airborne contamination must be done with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

4.3.1.11 Accidents—Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.1.3 Clearly label all samples as "POISON" and ship according to U.S. Department of Transportation regulations.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnels—2-L and 125-mL, with Teflon stopcock.

5.2.2 Concentrator tube, Kuderna-Danish—10mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.3 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.4 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.5 Snyder column, Kuderna-Danish—Two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.6 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.7 Chromatographic column—300 mm long × 10 mm ID, with Teflon stopcock and coarse frit filter disc at bottom.

5.2.8 Chromatographic column—400 mm long × 11 mm ID, with Teflon stopcock and coarse frit filter disc at bottom.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (±2 °C). The bath should be used in a hood.

5.5 GC/MS system:

5.5.1 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for capillary columns. Either split, splitless, or on-column injection techniques may be employed, as long as the requirements of Section 7.1.1 are achieved.

5.5.2 Column—60 m long × 0.25 mm ID glass or fused silica, coated with SP-2330 (or equivalent) with a film thickness of 0.2 µm. Any equivalent column must resolve 2, 3, 7, 8-TCDD from the other 21 TCDD isomers.[16]

5.5.3 Mass spectrometer—Either a low resolution mass spectrometer (LRMS) or a high resolution mass spectrometer (HRMS) may be used. The mass spectrometer must be equipped with a 70 V (nominal) ion source and be capable of aquiring m/z abundance data in real time selected ion monitoring (SIM) for groups of four or more masses.

5.5.4 GC/MS interface—Any GC to MS interface can be used that achieves the requirements of Section 7.1.1. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass surfaces can be deactivated by silanizing with dichlorodimethylsilane. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the ion source. A short piece of fused silica capillary can be used as the interface to overcome problems associated with straightening the exit end of glass capillary columns.

5.5.5 The SIM data acquired during the chromatographic program is defined as the Selected Ion Current Profile (SICP). The SICP can be acquired under computer control or as a real time analog output. If computer control is used, there must be software available to plot the SICP and report peak height or area data for any m/z in the SICP between specified time or scan number limits.

5.6 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of 2, 3, 7, 8-TCDD.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL. Wash the solution with methylene chloride and hexane before use.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid—Concentrated (ACS, sp. gr. 1.84).

6.5 Acetone, methylene chloride, hexane, benzene, ortho-xylene, tetradecane—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Alumina—Neutral, 80/200 mesh (Fisher Scientific Co., No. A-540 or equivalent). Before use, activate for 24 h at 130 °C in a foil-covered glass container.

6.8 Silica gel—High purity grade, 100/120 mesh (Fisher Scientific Co., No. S-679 or equivalent).

6.9 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Acetone should be used as the solvent for spiking solutions; ortho-xylene is recommended for calibration standards for split injectors; and tetradecane is recommended for splitless or on-colum injectors. Analyze stock internal standards to verify the absence of native 2,3,7,8-TCDD.

6.9.1 Prepare stock standard solutions of 2,3,7,8-TCDD (mol wt 320) and either $^{37}Cl_4$ 2,3,7,8-TCDD (mol wt 328) or $^{13}C_{12}$ 2,3,7,8-TCDD (mol wt 332) in an isolated area by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality solvent and dilute to volume in a 10-mL volumetric flask. When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.9.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store in an isolated refrigerator protected from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards or spiking solutions from them.

6.9.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.10 Internal standard spiking solution (25 ng/mL)—Using stock standard solution, prepare a spiking solution in acetone of either $^{13}C_{12}$ or $^{37}Cl_4$ 2,3,7,8-TCDD at a concentration of 25 ng/mL. (See Section 10.2)

6.11 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatograhic operating conditions equivalent to those given in Table 1 and SIM conditions for the mass spectrometer as described in Section 12.2 The GC/MS system must be calibrated using the internal standard technique.

7.1.1 Using stock standards, prepare calibration standards that will allow measurement of relative response factors of at least three concentration ratios of 2,3,7,8-TCDD to internal standard. Each calibration standard must be prepared to contain the internal standard at a concentration of 25 ng/mL. If any interferences are contributed by the internal standard at m/z 320 and 322, its concentration may be reduced in the calibration standards and in the internal standard spiking solution (Section 6.10). One of the calibration standards should contain 2,3,7,8-TCDD at a concentration near, but above, the MDL and the other 2,3,7,8-TCDD concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.2 Using injections of 2 to 5 μL, analyze each calibration standard according to Section 12 and tabulate peak height or area response against the concentration of 2,3,7,8-TCDD and internal standard. Calculate response factors (RF) for 2,3,7,8-TCDD using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = SIM response for 2,3,7,8-TCDD m/z 320.

A_{is} = SIM response for the internal standard, m/z 332 for $^{13}C_{12}$ 2,3,7,8-TCDD m/z 328 for $^{37}Cl_4$ 2,3,7,8-TCDD.

C_{is} = Concentration of the internal standard (μg/L).

C_s = Concentration of 2,3,7,8-TCDD (μg/L).

If the RF value over the working range is a constant (< 10% relative standard deviation, RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.1.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more 2,3,7,8-TCDD calibration standards. If the response for 2,3,7,8-TCDD varies from the predicted response by more than ±15%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

7.2 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.5, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The labbratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples with native 2,3,7,8-TCDD to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing 2,3,7,8-TCDD at a concentration of 0.100 μg/mL in acetone. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 0.100 μg/L (100 ng/L) by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in μg/L, and the standard deviation of the recovery (s) in μg/L, for 2,3,7,8-TCDD using the four results.

8.2.5 Compare s and ($\bar{X}$) with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If s exceeds the precision limit or $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for 2,3,7,8-TCDD. Locate and correct the source of the problem and repeat the test beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of 2,3,7,8-TCDD in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of 2,3,7,8-TCDD in the sample is not being checked against a limit specific to that parameter, the spike should be at 0.100 μg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 0.100 μg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of 2,3,7,8-TCDD. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of 2,3,7,8-TCDD. Calculate percent recovery (P) as 100(A−B)%T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for 2,3,7,8-TCDD with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[11] If spiking was performed at a concentration lower than 0.100 μg/L, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of 2,3,7,8-TCDD: (1) calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for X; (3) calculate the range for recovery at the spike concentration as (100 X'/T)±2.44(100 S'/T)%.[11]

8.3.4 If the recovery of 2,3,7,8-TCDD falls outside the designated range for recovery, a check standard must be analyzed as described in Section 8.4.

8.4 If the recovery of 2,3,7,8-TCDD fails the acceptance criteria for recovery in Section 8.3, a QC check standard must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the complexity of the sample matrix and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Section 8.2.1 or 8.3.2) to 1 L of reagent water.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of 2,3,7,8-TCDD. Calculate the percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) with the corresponding QC acceptance criteria found in Table 2. If the recovery of 2,3,7,8-TCDD falls outside the designated range, the laboratory performance is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for 2,3,7,8-TCDD in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the spandard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laborataory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevent performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices [12] should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C and protected from light from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[13] Field test kits are available for this purpose.

9.3 Label all samples and containers "POISON" and ship according to applicable U.S. Department of Transportation regulations.

9.4 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.[9]

10. Sample Extraction

Caution: When using this method to analyze for 2,3,7,8-TCDD, all of the following operations must be performed in a limited-access laboratory with the analyst wearing full protective covering for all exposed skin surfaces. See Section 4.2.

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 1.00 mL of internal standard spiking solution to the sample in the separatory funnel. If the final extract will be concentrated to a fixed volume below 1.00 mL (Section 12.3), only that volume of spiking solution should be added to the sample so that the final extract will contain 25 ng/mL of internal standard at the time of analysis.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.5 Assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator if the requirements of Section 8.2 are met.

10.6 Pour the combined extract into the K–D concentrator. Rinse the Erlenmeyer flask with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K–D apparatus and allow it to drain and cool for at least 10 min.

10.8 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Raise the temperature of the water bath to 85 to 90°C. Concentrate the extract as in Section 10.7, except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Set aside the K–D glassware for reuse in Section 10.14.

10.9 Pour the hexane extract from the concentrator tube into a 125-mL separatory funnel. Rinse the concentrator tube four times with 10-mL aliquots of hexane. Combine all rinses in the 125-mL separatory funnel.

10.10 Add 50 mL of sodium hydroxide solution to the funnel and shake for 30 to 60 s. Discard the aqueous phase.

10.11 Perform a second wash of the organic layer with 50 mL of reagent water. Discard the aqueous phase.

10.12 Wash the hexane layer with a least two 50-mL aliquots of concentrated sulfuric acid. Continue washing the hexane layer with 50-mL aliquots of concentrated sulfuric acid until the acid layer remains colorless. Discard all acid fractions.

10.13 Wash the hexane layer with two 50-mL aliquots of reagent water. Discard the aqueous phases.

10.14 Transfer the hexane extract into a 125-mL Erlenmeyer flask containing 1 to 2 g of anhydrous sodium sulfate. Swirl the flask for 30 s and decant the hexane extract into the reassembled K–D apparatus. Complete the quantitative transfer with two 10-mL hexane rinses of the Erlenmeyer flask.

10.15 Replace the one or two clean boiling chips and concentrate the extract to 6 to 10 mL as in Section 10.8.

10.16 Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Place the micro-K–D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 mL, remove the K–D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 mL of hexane.

Adjust the extract volume to 1.0 mL with hexane. Stopper the concentrator tube and store refrigerated and protected from light if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with GC/MS analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.17 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure.[5,6,7] However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure. Two cleanup column options are offered to the analyst in this section. The alumina column should be used first to overcome interferences. If background problems are still encountered, the silica gel column may be helpful.

11.2 Alumina column cleanup for 2,3,7,8-TCDD:

11.2.1 Fill a 300 mm long x 10 mm ID chromatographic column with activated alumina to the 150 mm level. Tap the column gently to settle the alumina and add 10 mm of anhydrous sodium sulfate to the top.

11.2.2 Preelute the column with 50 mL of hexane. Adjust the elution rate to 1 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1.0-mL sample extract onto the column using two 2-mL portions of hexane to complete the transfer.

11.2.3 Just prior to exposure of the sodium sulfate layer to the air, add 50 mL of 3% methylene chloride/97% hexane (V/V) and continue the elution of the column. Discard the eluate.

11.2.4 Next, elute the column with 50 mL of 20% methylene chloride/80% hexane (V/V) into a 500-mL K–D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction to 1.0 mL as in Section 10.16 and analyze by GC/MS (Section 12).

11.3 Silica gel column cleanup for 2,3,7,8-TCDD:

11.3.1 Fill a 400 mm long x 11 mm ID chromatographic column with silica gel to the 300 mm level. Tap the column gently to settle the silica gel and add 10 mm of anhydrous sodium sulfate to the top.

11.3.2 Preelute the column with 50 mL of 20% benzene/80% hexane (V/V). Adjust the elution rate to 1 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1.0-mL sample extract onto the column using two 2-mL portions of 20% benzene/80% hexane to complete the transfer.

11.3.3 Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of 20% benzene/80% hexane to the column. Collect the eluate in a clean 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction to 1.0 mL as in Section 10.16 and analyze by GC/MS.

12. GC/MS Analysis

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Other capillary columns or chromatographic conditions may be used if the requirements of Sections 5.5.2 and 8.2 are met.

12.2 Analyze standards and samples with the mass spectrometer operating in the selected ion monitoring (SIM) mode using a dwell time to give at least seven points per peak. For LRMS, use masses at m/z 320, 322, and 257 for 2,3,7,8-TCDD and either m/z 328 for $^{37}Cl_4$ 2,3,7,8-TCDD or m/z 332 for $^{13}C_{12}$ 2,3,7,8-TCDD. For HRMS, use masses at m/z 319.8965 and 321.8936 for 2,3,7,8-TCDD and either m/z 327.8847 for $^{37}Cl_4$ 2,3,7,8-TCDD or m/z 331.9367 for $^{13}C_{12}$ 2,3,7,8-TCDD.

12.3 If lower detection limits are required, the extract may be carefully evaporated to dryness under a gentle stream of nitrogen with the concentrator tube in a water bath at about 40 °C. Conduct this operation immediately before GC/MS analysis. Redissolve the extract in the desired final volume of ortho-xylene or tetradecane.

12.4 Calibrate the system daily as described in Section 7.

12.5 Inject 2 to 5 μL of the sample extract into the gas chromatograph. The volume of calibration standard injected must be measured, or be the same as all sample injection volumes.

12.6 The presence of 2,3,7,8-TCDD is qualitatively confirmed if all of the following criteria are achieved:

12.6.1 The gas chromatographic column must resolve 2,3,7,8-TCDD from the other 21 TCDD isomers.

12.6.2 The masses for native 2,3,7,8-TCDD (LRMS-m/z 320, 322, and 257 and HRMS-m/z 320 and 322) and labeled 2,3,7,8-TCDD (m/z 328 or 332) must exhibit a simultaneous maximum at a retention time that matches that of native 2,3,7,8-TCDD in the calibration standard, with the performance specifications of the analytical system.

12.6.3 The chlorine isotope ratio at m/z 320 and m/z 322 must agree to within ±10% of that in the calibration standard.

12.6.4 The signal of all peaks must be greater than 2.5 times the noise level.

12.7 For quantitation, measure the response of the m/z 320 peak for 2,3,7,8-TCDD and the m/z 332 peak for $^{13}C_{12}$ 2,3,7,8-TCDD or the m/z 328 peak for $^{37}Cl_4$ 2,3,7,8-TCDD.

12.8 Co-eluting impurities are suspected if all criteria are achieved except those in Section 12.6.3. In this case, another SIM analysis using masses at m/z 257, 259, 320 and either m/z 328 or m/z 322 can be performed. The masses at m/z 257 and m/z 259 are indicative of the loss of one chlorine and one carbonyl group from 2,3,7,8-TCDD. If masses m/z 257 and m/z 259 give a chlorine isotope ratio that agrees to within ±10% of the same cluster in the calibration standards, then the presence of TCDD can be confirmed. Co-eluting DDD, DDE, and PCB residues can be confirmed, but will require another injection using the appropriate SIM masses or full repetitive mass scans. If the response for $^{37}Cl_4$ 2,3,7,8-TCDD at m/z 328 is too large, PCB contamination is suspected and can be confirmed by examining the response at both m/z 326 and m/z 328. The $^{37}Cl_4$ 2,3,7,8-TCDD internal standard gives negligible response at m/z 326. These pesticide residues can be removed using the alumina column cleanup procedure.

12.9 If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst should employ additional cleanup procedures and reanalyze by GC/MS.

12.10 In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry is suggested.[8]

13. Calculations

13.1 Calculate the concentration of 2,3,7,8-TCDD in the sample using the response factor (RF) determined in Section 7.1.2 and Equation 2.

Equation 2:

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = SIM response for 2,3,7,8–TCDD at m/z 320.

A_{is} = SIM response for the internal standard at m/z 328 or 332.

I_s = Amount of internal standard added to each extract (μg).

V_o = Volume of water extracted (L).

13.2 For each sample, calculate the percent recovery of the internal standard by comparing the area of the m/z peak measured in the sample to the area of the same peak in the calibration standard. If the recovery is below 50%, the analyst should review all aspects of his analytical technique.

13.3 Report results in μg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[1] The MDL concentration listed in Table 1 was obtained using reagent water.[14] The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method was tested by 11 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.02 to 0.20 µg/L.[15] Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

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14. Wong, A.S. et al. "The Determination of 2,3,7,8-TCDD in Industrial and Municipal Wastewaters, Method 613, Part 1—Development and Detection Limits," G. Choudhay, L. Keith, and C. Ruppe, ed., Butterworth Inc., (1983).

15. "EPA Method Validation Study 23, Method 613 (2,3,7,8-Tetrachlorodibenzo-p-dioxin)," Report for EPA Contract 68-03-2863 (In preparation).

TABLE 1.—Chromatographic Conditions and Method Detection Limit

Parameter	Retention time (min)	Method detection limit (µg/L)
2,3,7,8,-TCDD	13.1	0.002

Column conditions: SP-2330 coated on a 60 m long x 0.25 mm ID glass column with hydrogen carrier gas at 40 cm/sec linear velocity, splitless injection using tetradecane. Column temperature held isothermal at 200°C for 1 min, then programmed at 8°C/min to 250 °C and held. Use of helium carrier gas will approximately double the retention time.

TABLE 2.—QC Acceptance Criteria—Method 613

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for X (µg/L)	Range for P, P_s (%)
2,3,7,8-TCDD	0.100	0.0276	0.0523–0.1226	45–129

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

X = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

Note.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE. 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 613

Parameter	Accuracy, as recovery, X′ (µg/L)	Single analyst, precision, s_r' (µ/L)	Overall precision, S′ (µ/g/L)
2,3,7,8-TCDD	0.86C+0.00145	$0.13\bar{X}+0.00129$	$0.19\bar{X}+0.00028$

X′ = Expected recovery for one or more measurements, of a sample containing a concentration of C, in µg/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
C = True value for the concentration, in µg/L.
$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

Method 624—Purgeables

1. Scope and Application

1.1 This method covers the determination of a number of purgeable organics. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Benzene	34030	71-43-2
Bromodichloromethane	32101	75-27-4
Bromoform	32104	75-25-2
Bromomethane	34413	74-83-9
Carbon tetrachloride	32102	56-23-5
Chlorobenzene	34301	108-90-7
Chloroethane	34311	75-00-3
2-Chloroethylvinyl ether	34576	110-75-8
Chloroform	32106	67-66-3
Chloromethane	34418	74-87-3
Dibromochloromethane	32105	124-48-1
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
1,1-Dichloroethane	34496	75-34-3
1,2-Dichloroethane	34531	107-06-2
1,1-Dichloroethane	34501	75-35-4
trans-1,2-Dichloroethene	34546	156-60-5
1,2-Dichloropropane	34541	78-87-5
cis-1,3-Dichloropropene	34704	10061-01-5
trans-1,3-Dichloropropene	34699	10061-02-6
Ethyl benzene	34371	100-41-4
Methylene chloride	34423	75-09-2
1,1,2,2-Tetrachloroethane	34516	79-34-5
Tetrachloroethene	34475	127-18-4
Toluene	34010	108-88-3
1,1,1-Trichloroethane	34506	71-55-6
1,1,2-Trichloroethane	34511	79-00-5
Trichloroethene	39180	79-01-6
Trichlorofluoromethane	34488	75-69-4
Vinyl chloride	39175	75-01-4

1.2 The method may be extended to screen samples for acrolein (STORET No. 34210, CAS No. 107-02-8) and acrylonitrile (STORET No. 34215, CAS No. 107-13-1), however, the preferred method for these two compounds in Method 603.

1.3 This is a purge and trap gas chromatographic/mass spectrometer (GC/MS) method applicable to the determination of the compounds listed above in municipal

SAS APPENDIX B

Modification of Method 613 to Form Method 613A and for application in Method 613E*

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*Developed for use in the EPA Effluent Guidelines Division Sampling and Analysis Program

Modifications of Method 613 to Form Method 613A and for Application in Method 613E

The following information is provided to clarify Methods 613A and Method 613E. Paragraph numbers in brackets [] reference paragraph numbers in EPA Method 613.

1. Compound Levels and Numbers

   a. The compound to be used for quantification by isotope dilution shall be carbon-13 labeled 2,3,7,8-TCDD ($^{13}C_{12}$). Fifty nanograms of $^{13}C_{12}$-2,3,7,8-TCDD shall be spiked into all water samples to result in a concentration of 50 ng/L for one liter samples and 5 ng/L for 10 liter samples. A labelled compound spiking solution replaces the "internal standard" spiking solution [613: 6.10] and is prepared using $^{13}C_{12}$-2,3,7,8-TCDD at 50 ug/mL. When extracted and concentrated to a volume of 50 uL, the extract concentration will be 1.0 ug/mL (1.0 ng/uL), assuming a 100 percent extraction efficiency.

   b. The EGD compound number to be used for reporting $^{13}C_{12}$-2,3,7,8-TCDD shall be 429.

   c. Chlorine-37 labeled 2,3,7,8-TCDD shall be spiked into each extract to yield a concentration of 1.0 ug/mL (1.0 ng/uL). the most efficient way to spike the extract is to prepare a solution of $^{37}Cl_4$-2,3,7,8-TCDD at a concentration of 1.0 ug/mL in isooctane, o-xylene, or tetradecane, and use 50 uL of this solution to redissolve the extract [613: 12.3]. $^{37}Cl_4$-2,3,7,8-TCDD is used as the internal standard for analysis of the $^{13}C_{12}$-2,3,7,8-TCDD so that recovery can be measured.

   d. The EGD compound number to be used for reporting $^{37}Cl_4$2,3,7,8-TCDD shall be 184.

2. Final Extract Volume

   The final extract volume for all samples shall be 0.05 mL (50 uL).

If the extract method cannot be concentrated to this volume, all cleanup steps in Method 613 [613: section 11] plus the additional cleanup step in Method 613E [613E: section 10] shall be employed. If the extract cannot then be concentrated to 50 uL, the Contractor shall notify the Sample Control Center by telephone (703/557-5040) within two working days.

3. Injection Volume

The injection volume for all calibration solutions [613: 7.1.2] and extracts [613: 12.5] shall be 2.0 ± 0.2 uL.

4. Interferences

If an interference precludes rigorous identification or quantitation of 2,3,7,8-TCDD at a level equal to or greater than 1 ug/mL (1 ng/uL) in an extract after all cleanup steps (see item 2, above) and alternate masses [613: 12.8] have been tried, the Contractor shall notify the Sample Control Center by telephone within two working days.

5. Calibration and Calibration Verification

a. A five-point calibration supercedes the three-point calibration in the Method [613: sections 6 and 7]. The calibration solutions to be used are as follows:

	Concentration of 2,3,7,8-TCDD (ug/mL and ng/uL Isotopically Labeled)		
Solution	$^{13}C_{12}$	$^{37}Cl_4$	Native
1	1.0	1.0	0.2
2	1.0	1.0	1.0
3	1.0	1.0	5.0
4	1.0	1.0	20
5	1.0	1.0	40

b. The response of 2,3,7,8-TCDD at m/z 320 is tabulated relative to $^{13}C_{12}$-2,3,7,8-TCDD at m/z 332 [613: 7.1.2]. The coefficient of variation (relative standard deviation) of the RF shall be less than 10 percent; otherwise a calibration curve is to be used.

c. The response of $^{13}C_{12}$-2,3,7,8-TCDD is tabulated relative to $^{37}Cl_4$-2,3,7,8-TCDD for all 5 calibration solutions. The coefficient of variation (relative standard deviation) of the RF shall be less than 20 percent; otherwise variables need better control and the test repeated.

d. Calibration verification [613: 7.1.3] is performed at 1 ug/mL (1ng/uL) for all TCDD isotopes once per 8-hour shift.

6. Initial and Ongoing Precision and Recovery

a. The QC check sample concentrate [613: 8.2.1] shall contain $^{13}C_{12}$-2,3,7,8-TCDD and a native 2,3,7,8-TCDD at 50 ng/mL each.

b. The specifications for initial precision and recovery from reagent water [613: 8.2-8.3] must be met and are as follows. For native 2,3,7,8-TCDD, the initial precision of the percent recoveries shall be less than 20 percent relative standard deviation, and the initial recoveries shall be between 75 and 116 percent by isotope dilution. For $^{13}C_{12}$-2,3,7,8-TCDD, the initial precision of the percent recoveries shall be less than 25 percent relative standard deviation, and the initial recoveries shall be between 50 and 130 percent by internal standard ($^{37}Cl_4$-2,3,7,8-TCDD).

c. Delete the requirement to spike and analyze 10 percent of all samples with native 2,3,7,8-TCDD [613: 8.1.2 and 8.4].

d. A test of ongoing precision and recovery is to be made by spiking 1 mL of reagent water for each set of samples started through the extraction process on a given 8-hour shift, to a maximum of six samples. Recovery of $^{13}C_{12}$-2,3,7,8-TCDD [613: section 13] shall be measured using $^{37}Cl_4$-2,3,7,8-TCDD as the internal standard. The ongoing precision and recovery shall be within the control limits specified [613: 8.3.1].

7. Final Extract Concentration

Change the final extract concentration [613: 10.2] to 1 mg/mL (1 ng/uL).

8. Accuracy Statements

Accuracy statements shall be developed using $^{13}C_{12}$-2,3,7,8-TCDD [613: 8.3.2] consisting of N, the average percent recovery of $^{13}C_{12}$-2,3,7,8-TCDD in all wastewater samples, and M, the coefficient of the percent recoveries of $^{13}C_{12}$-2,3,7,8-TCDD in all wastewater samples.

APPENDIX C

EXTENDED METHOD 613*

(EGD METHOD 613E)

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*Extended method developed for the analysis of 10 liter samples for 2,3,7,8-TCDD for use in the EPA Effluent Guidelines Division water and wastewater sampling and analysis program.

Appendix C   01 September 1983   Draft

Extension of EPA Method 613A to 10 Liter Samples to Detect Parts per Quadrillion (ppq) of 2,3,7,8-TCDD in Water*

1. Scope and Application

This procedure extends Method 613A to the ppq level for 2,3,7,8-TCDD in water by extraction of a 10 liter sample. The procedure is applied to relatively clean waters (drinking water, treated effluents, surface water) which yield extracts that can be concentrated to a final volume of 50-100 uL. Unless specified otherwise by this procedure, all requirements and specifications in Method 613A shall be met. Numbers in brackets [] reference paragraph numbers in Method 613, July 1982 Revision.

2. Apparatus and Materials [613: 5]

2.1. Sample bottle(s) [613: 5.1.1 and 5.1.2]--any combination of bottles which will result in collection of 10 liters of sample may be used.

2.2 Extraction apparatus--replace the separatory funnel [613: 5.2.1] with the following:

5.2.1E Extraction bottle or flask--11 to 19 liter glass vessel capable of being stirred by a magnetic stirring bar.

5.2.1.1E Magnetic stirrer and bar capable of stirring water in the vessel in 5.2.1E.

2.3 Change the volume of the K-D flask [613: 5.2.3] to 1000 mL.

3. Regeants [613:6]

3.1 Change the concentration of the 25 ng/mL internal standard spiking solution [613: 6.10] to 50 ng/mL.

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*Adapted from EPA Region V "Dow Task Force Report" Appendix B.

4. QA/QC [613: 8]

   4.1 Change the concentration of the QC check sample concentrate [613: 8.2.1] to 50 ng/mL.

   4.2 Change the volume of the initial 1000 mL aliquots [613: 8.2.2] to 10 liters.

   4.3 Change the volume of the 1 liter blank [613: 8.5] to 10.0 liters.

5. Extraction and Concentration [613: 10]

   5.1 Change "two liter separatory funnel" [613: 10.1 and 10.2] to "extraction vessel" (section 5.2.1E).

   5.2 Change "25 ng/mL" [613: 10.2] to "one ug/mL".

   5.3 Replace the extraction and transfer procedures [613: 10.3, 10.4 and 10.6] with the following:

10.3E Extraction by magnetic stirring

10.3.1E Stir the sample plus internal standard at 50-150 rpm for 25-35 minutes.

10.3.2E Add one liter of hexane to the extraction vessel.

10.3.3E Stir the mixture at 50-150 rpm for 16-24 hours.

10.4E Transfer the hexane to a 1.5-3 liter bottle or flask using a 100-500 mL pipet. If necessary, add reagent water to the extraction vessel to force the extract into the neck for easy withdrawal. If residual water is present in the extract, add sufficient sodium sulfate to remove the water.

10.6E Pour the extract into the K-D concentrator. Rinse the bottle or flask (10.4E) with 50-100 mL hexane and add to the K-D flask.

5.4 Prewet the column [613: 10.7] with hexane.

5.5 Change the bath temperature [613:10.7] to 85-95°C.

5.6 Change the time for concentration [613: 10.7] to 30-60 minutes.

5.7 Change the apparent volume [613: 10.7] to 5 mL.

5.8 Delete the hexane exchange [613: 10.8].

5.9 Delete the extract adjustment to 1.0 mL [613: 10.16].

5.10 Change the 1000 mL graduated cylinder and 5 mL requirements [613: 10.7] to any vessel which will perit accurate measurement of 10 liters within ±5 percent.

6. Cleanup and Separation [613:11]

6.1 Change the final volume requirement [613: 11.3.4] to 0.5 to 2 mL and delete analysis of the extract at this volume.

7. GC/MS Analysis [613: 12]

7.1 Use the blowdown procedure [613: 12.3] to bring the final volume of extract to 50 uL.

8. Calculations [613: 13]

8.1 Change the recovery specification [613: 13.2] to 20 percent.

9. Method Performance [613: 14]

9.1 Change the detection limit [613: 14.1 and table 1] to 100 pg/L (ppq).

9.2 Change the recovery and relative standard deviation [613: 14.2 and tables 2 and 3] to 84 percent and 9 percent, respectively for reagent water.

10. Additional Cleanup*

This cleanup procedure is to be used for extracts which do not concentrate to 50 uL or when an interference is present at m/z 320, 328, or 332 for 2,3,7,8-TCDD, $^{37}Cl_4$-TCDD, or $^{13}C_{12}$-TCDD as evidenced by improper isotope ratios, and only after all other cleanup procedures in the method have been shown to be ineffective.

10.1 Prepare 18 percent Carbopak C on Celite 545 by thoroughly mixing 3.6 grams of Carbopak C (80/100) mesh and 16.4 grams of Celite 545 in a 40 mL vial. Activate at 130°C for six hours. Store in a dessicator.

10.2 Prepare a column using a 5-3/4 in. x 5 mm i.d. disposable pipet fitted with a small plug of glass wool.

10.3 Using a vacuum aspirator attached to the pointed end of the pipet, add Carbopak/Celite mix until a 2 cm column is obtained.

10.4 Pre-elute the column with 2mL of tolune followed by one mL of cyclohexane:methylene chloride (1:1) and 2 mL hexane. While the column is still wet with hexane, add the extract. Elute with two 1-mL aliquots of hexane, one mL cyclohexane:methylene chloride (1:1), and one mL methylene chloride:methanol:benzene (75:20:5).

*Adapted from EPA Region VII procedure for "Determination of 2,3,7,8-TCDD in Soil and Sediment.

10.5 Elute with the TCDD fraction with 2 mL toluene.

10.6 Store the 2mL extract in a freezer until ready for analysis.

10.7 Just before analysis, reduce the volume to near dryness and add isooctane to obtain a final volume of 50 uL.

NOTE: For quality assurance purposes, the initial [613: 8.2.2] and on-going [613: 8.4] reagent water aliquots shall be taken through the entire cleanup procedure used with samples. Recoveries for 2,3,7,8-TCDD by isotope dilution shall be 70-130 percent, and recoveries for labelled TCDD shall be 20-200 percent by the internal standard method using $^{37}Cl_4$-2,3,7,8-TCDD spiked into the extract as the internal standard for reference. Each batch of cleanup material (silica gel, alumina, Carbopak/Celite, etc) shall be tested to insure recovery within the limits above.

EPA METHOD
NO. 8280M

GC/MS Conditions

Gas Chromatography:

Capillary Column:
a. Manufacturer - J&W Scientific
b. Liquid phase - DB-5
c. Length - 60 m
d. I.D - 0.25 mm
e. film thickness - 0.25 microns

Carrier gas : Helium
Head pressure : 28 psi
Flow thru column: 1 to 2 ml/min.
Injection type : Splitless for 30 sec.

Initial isothermal temperature :150 deg C for 30 sec.
Initial temperature program rate: to 190 deg C ballistically
Final temperature program rate : to 300 deg C @ 3 deg/min

Mass Spectrometry:

Ionization mode : EI, positive ion
Reactant gas : N/A
Resolution : 5000
Scan mode : selected ion recording
Switching mode : voltage
Reference standard: PFK

SLUDGE SAMPLES

1)100ML round bottom flask + boiling chip + sample (~2g) + 200ul water + 200ul spiking solution + 50ml toluene.

2) Connect Dean/stark trap and heat apparatus to 100deg C until volume of water collected in the resevoir is a constant value.

3) Disconnect apparatus , pipet toluene in side tube to sample round bottom flask, discard water.
Rinse apparatus with 2 X 5ml toluene.

4) Filter sample though #54 Whatman into a clean round bottom flask. Rinse 1 st flask + filter with 2 X 5 ml toluene . Rotary evaporate to ~1ml.

5) go to step #9)

WATER SAMPLES

1)Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

2) Add internal standard spiking solution to the sample in the separatory funnel.

3) Add 60ml methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to-complete the phase separation. The optimum technique depends on the sample, but may include stirring, filtering of the emulsion though glass wool, centifugation, or other physical methods.
Collect the methylene chloride extract in a 250ml Erlenmeyer flask.

4) Added a second 60 ml volume of methylene chloride to the sample bottle and repeat the extraction procedure, combining the extract in the erlenmeyer flask. Perform a third extraction in the same manner.

5) Assemble a Kuderna-Danish (KD) concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporative flask.

6) Pour the combined extract into the KD concentrator. Rinse the erlenmeyer flask with 3 X 10ml of methylene chloride to complete the quantitative transfer.

7) Add one or more clean boiling chips to the evaporator and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml of methylene chloride to the top. Place the KD apparatus on a hot water bath (60-65 deg C) .so that the concentator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of the liquid reaches 1 ml remove the KD apparatus and allow to cool and drain for at least 10 min.

8) Add 50 ml hexane and concentrate to 1 ml.

PURIFICATION

9)Transfer to 250 ml separatory funnel with 5 X 5 ml hexane. Add 50 ml 5% NaCl solution, shake for 2 min and discard aqueous (bottom) layer.
10) Add 40 ml 20% KOH (w/v) , shake for 2 min . discard aqueous layer (bottom) repeat the base washing until no color is visible the the bottom layer-- a maximum of 4 times
11) Add 40 ml water shake for 2 min , discard aqueous layer
12) Add 40 ml concentrated sulfuric acid, shake for 2 min , discard bottom layer. Repeat acid washing until no visible color is in the bottom layer. A maximum or 4 times.
13) Add 40 ml water (care) shake for 2 min , discard bottom layer.
14 Filter upper layer though anhydrous sodium sulfate. Rinse with 2 X 5 ml hexane into 50 ml round bottom flask.
14) Rotary evaporate to near dryness a <35 deg C
15) Add 2 ml hexane to sample and have ready to load
    25 ml pipet column with glasswool plug
    +4g purified sodium sulfate (next page)
    + 4g Woelm super neutral alumnia (desiccated)
    + 4g sodium sulfate
Wash with 10 ml hexane
When hexane layer reaches surface add sample the add 4 ml hexane rinse(2 X 2) NOTE.. NEVER ALLOW SOLUTIONS TO GO BELOW SURFACE OF SODIUM SULFATE.
Discard all the above elutants

Fr #1 = (into scintillation vial)
    10 ml 8%(v/v) methylene chloride/ hexane --(hold)
Fr #2 15ml 60%(v/v) methylene chloride/ hexane into a 50 ml round bottom flask
Rotary evaporate to near dryness.
16) Prepare carbon column
    9.5g Biosil A silica Gel 24 hrs @ 225 deg C
    +0.5g AX-21 carbon
    mix for 1 hour
    2ml disposable pipet-broken at 1.8ml mark- glasswool plug at 0.0 mark
+ Biosil A silica gel to 0.1ml mark
+ carbon/Biosil A mixture to 0.45ml mark
+ glasswool plug
  Prewash column with :- 0.5ml 50% benzene/ methylene chloride .
 9.5 ml 50% benzene/ methylene chloride.
10 ml toluene
add 1ml hexane
17) add 1 ml hexane
load sample 0.2-0.4 ml in hexane
rinse with 2 X 0.2 ml hexane
add 5.0 ml hexane
add 10 ml 50 % benzene/ hexane
18) Turn column upside down
Elute with 10 ml toluene
transfer to sample tube and evaporate to near dryness with nitrogen

Col A 50 gr A-540 basic alumina , activated 16-72hrs @ 130deg C
purified sodium sulfate on top (1-2cm)

Load sample on column with ~1ml hexane
Rinse 2 X 0.5ml hexane.
Wash with 250ml hexane-discard
elute with 250ml 35% methylene chloride/hexane-collecting in 500 ml round bottom flask.
Rotary evaporate to near dryness- add 10 ml hexane reevaporate ## . Add 2ml 2% methylene chloride/hexane to sample load onto column B.

Col B 25 ml pipet with glasswool plug.
6 gm A-540 basic alumina activated 16-72hrs @ 130 deg C
1cm sodium sulfate on top

Load sample on column
Rinse 2 X 1ml 2% methylene chloride/hexane
Wash with 60ml 2% methlene chloride/hexane---discard
add 60 ml 20% methyle chloride/hexane collecting in a 100ml round bottom flask.
Rotary evaporate to near dryness- add 10 ml hexane reevaporate to near dryness. ##
Make volume to 2ml with hexane.

rotary evaporation tempeature 30 deg C

Col 1

25 ml pipet with glasswool plug
1gm Silica gel activated 16-72hrs 130deg C
2gm Silica gel with 1N NaOH (2:1)
1gm Silica gel
12 gm Silica gel with conc sulfuric acid(3:2)
2gm Silica gel
1 cm sodium sulfate on top

Col 2 Directly under col 1
25ml pipet with glasswool plug
6gm A-948 Alumina with 10% water activated 16-72 hrs 130deg C.
1cm sodiun sulfater on top

Load sample onto column 1
Rinse 2 X 1ml hexane
Wash with 162ml hexane --discard.
Remove column 1 .
Onto column 2 add 20ml 1% methylene chloride/hexane--save
Add 20ml 20% methylene chloride/ hexane.
Evaporate----------Finished--------

METHOD 8280

THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

1.0 SCOPE AND APPLICATION

1.1 This method is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) in chemical wastes including still bottoms, fuel oils, sludges, fly ash, reactor residues, soil and water.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposed quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water. Actual values have been shown to vary by homologous series and, to a lesser degree, by individual isomer. The total detection limit for each CDD/CDF homologous series is determined by multiplying the detection limit of a given isomer within that series by the number of peaks which can be resolved under the gas chromatographic conditions.

1.3 Certain 2,3,7,8-substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Special instructions are included which measure 2,3,7,8-substituted congeners.

1.4 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.5 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. A laboratory planning to use these compounds should prepare a disposal plan to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450). Additional safety instructions are outlined in Appendix B.

2.0 SUMMARY OF THE METHOD

2.1 This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) techniques.

2.2 If interferents are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

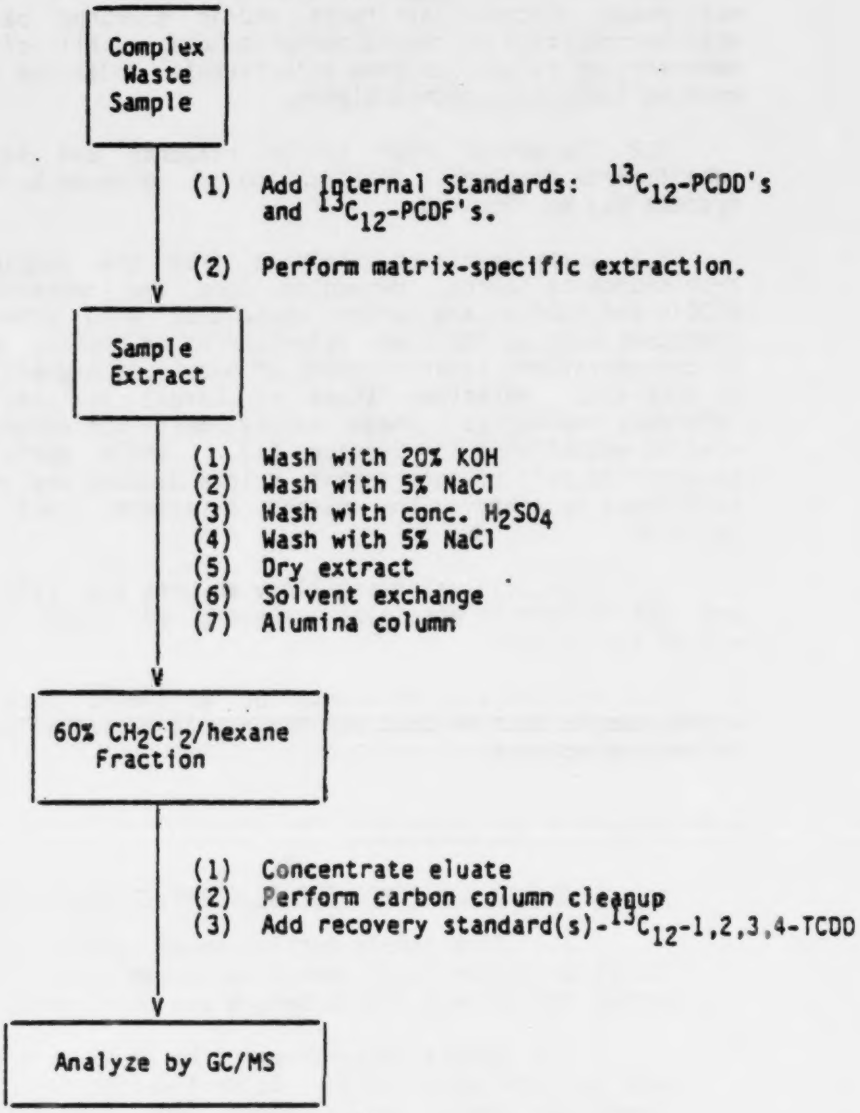
Complex Waste Sample
(1) Add Internal Standards: $^{13}C_{12}$-PCDD's and $^{13}C_{12}$-PCDF's.
(2) Perform matrix-specific extraction.
Sample Extract
(1) Wash with 20% KOH
(2) Wash with 5% NaCl
(3) Wash with conc. H_2SO_4
(4) Wash with 5% NaCl
(5) Dry extract
(6) Solvent exchange
(7) Alumina column
60% CH_2Cl_2/hexane Fraction
(1) Concentrate eluate
(2) Perform carbon column cleanup
(3) Add recovery standard(s)-$^{13}C_{12}$-1,2,3,4-TCDD
Analyze by GC/MS

Figure 1. Method 8280 flow chart for sample extraction and cleanup as used for the analysis of PCDD's and PCDF's in complex waste samples.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 6-3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit (Section 11.6) stated in Table 8.

3.4 High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers.

3.5 Aqueous samples cannot be aliquoted from sample containers. The entire sample must be used and the sample container washed/rinsed out with the extracting solvent.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment for discrete or composite sampling:

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be acid washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil, used with the shiny side toward the sample, may be substituted for Teflon if the sample is not corrosive. Apply tape around cap to completely seal cap to bottom.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ$C). The bath should be used in a hood.

4.3 Gas chromatograph/mass spectrometer data system:

4.3.1 **Gas chromatograph:** An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Fused silica capillary columns are required. As shown in Table 1, three columns were evaluated using a column performance check mixture containing 1,2,3,4-TCDD, 2,3,7,8-TCDD, 1,2,3,4,7 PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,7,8-TCDF.

The columns include the following: (a) 50-m CP-Sil-88 programmed 60°-190° at 20°/minute, then 190°-240° at 5°/minute; (b) DB-5 (30-m x 0.25-mm I.D.; 0.25-um film thickness) programmed 170° for 10 minutes, then 170°-320° at 8°/minute, hold at 320°C for 20 minutes; (c) 30-m SP-2250 programmed 70°-320° at 10°/minute. Column/conditions (a) provide good separation of 2,3,7,8-TCDD from the other TCDD's at the expense of longer retention times for higher homologs. Column/conditions (b) and (c) can also provide acceptable separation of 2,3,7,8-TCDD. Resolution of 2,3,7,8-TCDD from the other TCDD's is better on column (c), but column (b) is more rugged, and may provide better separation from certain classes of interferents. Data presented in Figure 2 and Tables 1 to 8 of this Method were obtained using a DB-5 column with temperature programming described in (b) above. However, any capillary column which provides separation of 2,3,7,8-TCDD from all other TCDD isomers equivalent to that specified in Section 6.3 may be used; this separation must be demonstrated and documented using the performance test mixture described in Paragraph 6.3.

4.3.3 **Mass spectrometer:** A low resolution instrument is specified, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM) for at least 11 ions simultaneously, with a cycle time of 1 sec or less. Minimum integration time for SIM is 50 ms per m/z. The use of systems not capable of monitoring 11 ions simultaneously will require the analyst to make multiple injections.

4.3.4 **GC/MS interface:** Any GC-to-MS interface that gives an acceptable calibration response for each analyte of interest at the concentration required and achieves the required tuning performance criteria (see Paragraphs 6.1.-6.3) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended; care must be taken not to expose the end of the column to the electron beam.

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow for the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot is defined as an Selected Ion Current Profile (SICP). Software must also be able to integrate the abundance, in any SICP, between specified time or scan number limits.

4.4 Pipets-Disposable, Pasteur, 150-mm long x 5-mm I.D. (Fisher Scientific Company, No. 13-678-6A, or equivalent).

4.4.1 Pipet, disposable, serological 10-mL (American Scientific Products No. P4644-10, or equivalent) for preparation of the carbon column specified in Paragraph 4.19.

4.5 Amber glass bottle (500-mL, Teflon-lined screw-cap).

4.6 Reacti-vial 2-mL, amber glass (Pierce Chemical Company). These should be silanized prior to use.

4.7 500-mL Erlenmeyer flask (American Scientific Products Cat. No. f4295 500f0) fitted with Teflon stoppers (ASP No. s9058-8, or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049, or equivalent).

4.9 125-mL and 2-L Separatory Funnels (Fisher Scientific Company, No. 10-437-5b, or equivalent).

4.10 500-mL Kuderna-Danish fitted with a 10-mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02, or equivalent).

4.11 Teflon boiling chips (Berghof/American Inc., Main St., Raymond, New Hampshire 03077, No. 15021-450, or equivalent). Wash with hexane prior to use.

4.12 300-mm x 10.5-mm glass chromatographic column fitted with Teflon stopcock.

4.13 15-mL conical concentrator tubes (Kontes No. K-288250, or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20, or equivalent).

4.15 Nitrogen blowdown apparatus (N-Evap (reg. trademark) Analytical Evaporator Model 111, Organomation Associates Inc., Northborough, Massachusetts or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.16 Microflex conical vials 2.0-mL (Kontes K-749000, or equivalent).

4.17 Filter paper (Whatman No. 54, or equivalent). Glass fiber filters or glass wool plugs are also recommended.

4.18 Solvent reservoir (125-mL) Kontes: (special order item) 12.5-cm diameter, compatible with gravity carbon column.

4.19 Carbon column (gravity flow): Prepare carbon/silica gel packing material by mixing 5 percent (by weight) active carbon AX-21 (Anderson Development Co., Adrain, Michigan), pre-washed with methanol and dried *in vacuo* at 110°C and 95 percent (by weight) Silica gel (Type 60, EM reagent 70 to 230 mesh, CMS No. 393-066) followed by activation of the mixture at 130° for 6 hr. Prepare a 10-mL disposable serological pipet by cutting off each end to achieve a 4-in. column. Fire polish both ends; flare if desired. Insert a glass-wool plug at one end and pack with 1 g of the carbon/silica gel mixture. Cap the packing with a glass-wool plug. (Attach reservoir to column for addition of solvents).

Option: Carbon column (HPLC): A silanized glass HPLC column (10 mm x 7 cm), or equivalent, which contains 1 g of a packing prepared by mixing 5 percent (by weight) active carbon AX-21, (Anderson Development Co., Adrian, Michigan), washed with methanol and dried *in vacuo* at 110°C, and 95 percent (by weight) 10 um silica (Spherisorb S10W from Phase Separations, Inc., Norwalk, Connecticut). The mixture must then be stirred and sieved through a 38-um screen (U.S. Sieve Designation 400-mesh, American Scientific Products, No. S1212-400, or equivalent) to remove any clumps.[1]

4.20 HPLC pump with loop valve (1.0 mL) injector to be used in the optional carbon column cleanup procedure.

4.21 Dean-Stark trap, 5- or 10-mL with T joints, (Fisher Scientific Company, No. 09-146-5, or equivalent) condenser and 125-mL flask.

4.22 Continuous liquid-liquid extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915; or equivalent.).

4.23 Roto-evaporator, R-110. Buchi/Brinkman - American Scientific No. E5045-10; or equivalent.

5.0 REAGENTS

5.1 Potassium hydroxide (ASC): 20 percent (w/v) in distilled water.

5.2 Sulfuric acid (ACS), concentrated.

5.3 Methylene chloride, hexane, benzene, petroleum ether, methanol, tridecane, isooctane, toluene, cyclohexane. Distilled in glass or highest available purity.

5.4 Prepare stock standards in a glovebox from concentrates or neat materials. The stock solutions (50 ppm) are stored in the dark at 4°C, and checked frequently for signs of degradation or evaporation, especially just prior to the preparation of working standards.

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[1] The carbon column preparation and use is adapted from W. A. Korfmacher, L. G. Rushing, D. M. Nestorick, H. C. Thompson, Jr., R. K. Mitchum, and J. R. Kominsky, Journal of High Resolution Chromatography and Chromatography Communications, 8, 12-19 (1985).

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade): Extracted by manual shaking with several portions of hexane and dried at 100°C.

5.8 Sodium chloride - (analytical reagent), 5 percent (w/v) in distilled water.

6.0 CALIBRATION

6.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. The other type, routine calibration, consists of analyzing the column performance check solution and a concentration calibration solution of 500 ng/mL (Paragraph 6.2). No samples are to be analyzed until acceptable calibration as described in Paragraphs 6.3 and 6.6 is demonstrated and documented.

6.2 Initial calibration:

6.2.1 Prepare multi-level calibration standards[2] keeping one of the recovery standards and the internal standard at fixed concentrations (500 ng/mL). Additional internal standards ($^{13}C_{12}$-OCDD 1,000 ng/mL) are recommended when quantification of the hepta- and octa-isomers is required. The use of separate internal standards for the PCDF's is also recommended. Each calibration standard should contain the following compounds:

2,3,7,8-TCDD,
1,2,3,7,8-PeCDD or any available 2,3,7,8,X-PeCDD isomer,
1,2,3,4,7,8-HxCDD or any available 2,3,7,8,X,Y-HxCDD isomer,
1,2,3,4,6,7,8-HpCDD or any available 2,3,7,8,X,Y,Z-HpCDD isomer,

2,3,7,8-TCDF
1,2,3,7,8,PeCDF or any available 2,3,7,8,X-PeCDF isomer,
1,2,3,4,7,8-HxCDF or any available 2,3,7,8,X,Y,HxCDF isomer,
1,2,3,4,6,7,8-HpCDF or any available 2,3,7,8,X,Y,Z-HpCDF isomer,

OCDD, OCDF, $^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-OCDD.

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[2] $^{13}C_{12}$-labeled analytes are available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper quantification requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required consistent with the technique of isotopic dilution.

Recommended concentration levels for standard analytes are 200, 500, 1,000, 2,000, and 5,000 ng/mL. These values may be adjusted in order to insure that the analyte concentration falls within the calibration range. Two uL injections of calibration standards should be made. However, some GC/MS instruments may require the use of a 1-uL injection volume; if this injection volume is used then all injections of standards, sample extracts and blank extracts must also be made at this injection volume. Calculation of relative response factors is described in Paragraph 11.1.2. Standards must be analyzed using the same solvent as used in the final sample extract. A wider calibration range is useful for higher level samples provided it can be described within the linear range of the method, and the identification criteria defined in Paragraph 10.4 are met. All standards must be stored in an isolated refrigerator at 4°C and protected from light. Calibration standard solutions must be replaced routinely after six months.

6.3 Establish operating parameters for the GC/MS system; the instrument should be tuned to meet the isotopic ratio criteria listed in Table 3 for PCDD's and PCDF's. Once tuning and mass calibration procedures have been completed, a column performance check mixture[3] containing the isomers listed below should be injected into the GC/MS system:

TCDD	1,3,6,8; 1,2,8,9; 2,3,7,8; 1,2,3,4; 1,2,3,7; 1,2,3,9
PeCDD	1,2,4,6,8; 1,2,3,8,9
HxCDD	1,2,3,4,6,9; 1,2,3,4,6,7
HpCDD	1,2,3,4,6,7,8; 1,2,3,4,6,7,9
OCDD	1,2,3,4,6,7,8,9
TCDF	1,3,6,8; 1,2,8,9
PeCDF	1,3,4,6,8; 1,2,3,8,9
HxCDF	1,2,3,4,6,8; 1,2,3,4,8,9
HpCDF	1,2,3,4,6,7,8; 1,2,3,4,7,8,9
OCDF	1,2,3,4,6,7,8,9

Because of the known overlap between the late-eluting tetra-isomers and the early-eluting penta-isomers under certain column conditions, it may be necessary to perform two injections to define the TCDD/TCDF and PeCDD/PeCDF elution windows, respectively. Use of this performance check mixture will enable the following parameters to be checked: (a) the retention windows for each of the homologues, (b) the GC resolution of 2,3,7,8-TCDD and 1,2,3,4-TCDD, and (c) the relative ion abundance criteria listed for PCDD's and PCDF's in Table 3. GC column performance should be checked daily for resolution and peak shape using this check mixture.

The chromatographic peak separation between 2,3,7,8-TCDD and 1,2,3,4-TCDD must be resolved with a valley of ≤ 25 percent, where

$$\text{Valley Percent} = (x/y)\ (100)$$

x = measured as in Figure 2
y = the peak height of 2,3,7,8-TCDD

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[3] Performance check mixtures are available from Brehm Laboratory, Wright State University, Dayton, Ohio.

It is the responsibility of the laboratory to verify the conditions suitable for maximum resolution of 2,3,7,8-TCDD from all other TCDD isomers. The peak representing 2,3,7,8-TCDD should be labeled and identified as such on all chromatograms.

6.4 Acceptable SIM sensitivity is verified by achieving a minimum signal-to-noise ratio of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/mL calibration standard.

6.5 From injections of the 5 calibration standards, calculate the relative response factors (RRF's) of analytes vs. the appropriate internal standards, as described in Paragraph 11.1.2. Relative response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards.

6.6 For each analyte calculate the mean relative response factor (RRF), the standard deviation, and the percent relative standard deviation from triplicate determinations of relative response factors for each calibration standard solution.

6.7 The percent relative standard deviations (based on triplicate analysis) of the relative response factors for each calibration standard solution should not exceed 15 percent. If this condition is not satisfied, remedial action should be taken.

6.8 The Laboratory must not proceed with analysis of samples before determining and documenting acceptable calibration with the criteria specified in Paragraphs 6.3 and 6.7.

6.9 Routine calibration:

6.9.1 Inject a 2-uL aliquot of the column performance check mixture. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the ions being monitored.

NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution. The column performance check solution must be run at the beginning and end of a 12 hr period. If the contractor laboratory operates during consecutive 12-hr periods (shifts), analysis of the performance check solution at the beginning of each 12-hr period and at the end of the final 12-hr period is sufficient.

Determine and document acceptable column performance as described in Paragraph 6.3.

6.9.2 Inject a 2-uL aliquot of the calibration standard solution at 500 ng/mL at the beginning of a 2-hr period. Determine and document acceptable calibration as specified in Paragraph 6.3, i.e., SIM sensitivity and relative ion abundance criteria. The measured RRF's of all analytes must be within ±30 percent of the mean values established by initial analyses of the calibration standard solutions.

7.0 QUALITY CONTROL

7.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank that all glassware and reagents are interferent-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

7.2 A laboratory "method blank" must be run along with each analytical batch (20 or fewer samples). A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a sample. The method blank is also dosed with the internal standards. For water samples, one liter of deionized and/or distilled water should be used as the method blank. Mineral oil may be used as the method blank for other matrices.

7.3 The laboratory will be expected to analyze performance evaluation samples as provided by the EPA on a periodic basis throughout the course of a given project. Additional sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and acceptable performance must be demonstrated before sample analyses can resume.

7.4 Samples may be split with other participating labs on a periodic basis to ensure interlaboratory consistency. At least one sample per set of 24 must be run in duplicate to determine intralaboratory precision.

7.5 Field duplicates (individual samples taken from the same location at the same time) should be analyzed periodically to determine the total precision (field and lab).

7.6 Where appropriate, "field blanks" will be provided to monitor for possible cross-contamination of samples in the field. The typical "field blank" will consist of uncontaminated soil (background soil taken off-site).

7.7 GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hr period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

7.8 Before using any cleanup procedure, the analyst must process a series of calibration standards (Paragraph 6.2) through the procedure to validate elution patterns and the absence of interferents from reagents. Both alumina column and carbon column performance must be checked. Routinely check the 8 percent CH_2Cl_2/hexane eluate of environmental extracts from the alumina column for presence of target analytes.

NOTE: This fraction is intended to contain a high level of interferents and analysis near the method detection limit may not be possible.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing, other potential sources of contamination which may absorb the target analytes.

8.2 All samples must be stored at 4°C, extracted within 30 days and completely analyzed within 45 days of collection.

9.0 EXTRACTION AND CLEANUP PROCEDURES

9.1 Internal standard addition. Use a sample aliquot of 1 g to 1,000 mL (typical sample size requirements for each type of matrix are provided in Paragraph 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD, and any other material which is to be used as an internal standard, (Paragraph 6.2). All samples should be spiked with at least one internal standard, for example, $^{13}C_{12}$-2,3,7,8-TCDD, to give a concentration of 500 ng/mL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 uL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD, assuming 100% recovery. Adoption of different calibration solution sets (as needed to achieve different quantification limits for different congeners) will require a change in the fortification level. Individual concentration levels for each homologous series must be specified.

9.2 Extraction

9.2.1 Sludge/fuel oil. Extract aqueous sludge samples by refluxing a sample (e.g. 2 g) with 50 mL of toluene (benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through a fiber filter, or equivalent, into a 100-mL round bottom flask. Rinse the filter with 10 mL of toluene, combine the extract and rinsate. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Step 9.2.4.

9.2.2 Still bottom. Extract still bottom samples by mixing a sample (e.g., 1.0 g) with 10 mL of toluene (benzene) in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50-mL round bottom flask. Rinse the beaker and filter with 10 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C while connected to a water aspirator. Proceed with Step 9.2.4.

9.2.3 Fly ash. Extract fly ash samples by placing a sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with 100 mL of toluene (benzene) and extract for 16 hr using a three cycle/hour schedule. Cool and filter the toluene extract through a glass fiber filter paper into a 500-mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C. Proceed with Step 9.2.4.

9.2.4 Transfer the residue to a 125-mL separatory funnel using 15 mL of hexane. Rinse the flask with two 5-mL aliquots of hexane and add the rinses to the funnel. Shake 2 min with 50 mL of 5% NaCl solution, discard the aqueous layer and proceed with Step 9.3.

9.2.5 Soil. Extract soil samples by placing the sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a 500-mL Erlenmeyer flask fitted with a Teflon stopper. Add 20 mL of methanol and 80 mL of petroleum ether, in that order, to the flask. Shake on a wrist-action shaker for two hr. The solid portion of sample should mix freely. If a smaller soil aliquot is used, scale down the amount of methanol proportionally.

9.2.5.1 Filter the extract from Paragraph 9.2.5 through a glass funnel fitted with a glass fiber filter and filled with anhydrous sodium sulfate into a 500-mL Kuderna-Danish (KD) concentrator fitted with a 10-mL concentrator tube. Add 50 mL of petroleum ether to the Erlenmeyer flask, restopper the flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Repeat this procedure with two additional 50-mL aliquots of petroleum ether. Wash the sodium sulfate in the funnel with two additional 5-mL portions of petroleum ether.

9.2.5.2 Add a Teflon or PFTE boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70°C water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow it to cool for 5 min.

9.2.5.3 Add 50 mL of hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 min.

9.2.5.4 Remove and invert the Snyder column and rinse it down into the KD with two 1-mL portions of hexane. Decant the contents of the KD and concentrator tube into a 125-mL separatory funnel. Rinse the KD with two additional 5-mL portions of hexane, combine. Proceed with Step 9.3.

9.2.6 Aqueous samples: Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume.

Pour the entire sample (approximately 1-L) into a 2-L separatory funnel. Proceed with Step 9.2.6.1.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 sec to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL of methylene chloride to the distilling flask; add sufficient reagent water to ensure proper operation, and extract for 24 hr. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Paragraphs 9.2.6.1 and 9.2.6.2. Proceed with Paragraph 9.2.6.3.

9.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 sec to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500-mL Kuderna-Danish concentrator (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

9.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Paragraph 9.3.

9.3 In a 250-mL Separatory funnel, partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 min.

Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a maximum of four times). Strong base (KOH) is known to degrade certain PCDD/PCDF's, contact time must be minimized.

9.4 Partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard aqueous layer (bottom).

NOTE: Care should be taken due to the heat of neutralization and hydration.

9.5 Partition the solvent (15 mL hexane) against 40 mL of concentrated sulfuric acid. Shake for 2 min. Remove and discard the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

9.6 Partition the extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate into a 50-mL round bottom flask, wash the separatory funnel with two 15-mL portions of hexane, pour through the funnel, and combine the hexane extracts. Concentrate the hexane solution to near dryness with a rotary evaporator (35°C water bath), making sure all traces of toluene are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted).

9.7 Pack a gravity column (glass 300-mm x 10.5-mm), fitted with a Teflon stopcock, in the following manner:

Insert a glass-wool plug into the bottom of the column. Add a 4-g layer of sodium sulfate. Add a 4-g layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but should be stored in a sealed desiccator. Add a 4-g layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane and close the stopcock just prior to the exposure of the sodium sulfate layer to air. Discard the eluant. Check the column for channeling. If channeling is present discard the column. Do not tap a wetted column.

9.8 Dissolve the residue from Step 9.6 in 2 mL of hexane and apply the hexane solution to the top of the column. Elute with enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluant.

9.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane. Check by GC/MS analysis that no PCDD's or PCDF's are eluted in this fraction. See Paragraph 9.9.1.

9.8.2 Elute the PCDD's and PCDF's from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15-mL) concentrator tube.

9.9 Carbon column cleanup:

Prepare a carbon column as described in Paragraph 4.18.

9.9.1 Using a carefully regulated stream of nitrogen (Paragraph 4.15), concentrate the 8 percent fraction from the alumina column (Paragraph 9.8.1) to about 1 mL. Wash the sides of the tube with a small volume of hexane (1 to 2 mL) and reconcentrate to about 1 mL. Save this 8 percent concentrate for GC/MS analysis to check for breakthrough of PCDD's and PCDF's. Concentrate the 60 percent fraction (Paragraph 9.8.2) to about 2 to 3 mL. Rinse the carbon with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 mL of cyclohexane/methylene chloride (50:50 v/v) and 5 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine (this fraction may be used as a check on column efficiency). Now turn the column over and in the direction of forward flow elute the PCDD/PCDF fraction with 20 mL toluene.

NOTE: Be sure no carbon fines are present in the eluant.

9.9.2 **Alternate carbon column cleanup.** Proceed as in Section 9.9.1 to obtain the 60 percent fraction re-concentrated to 400 uL which is transferred to an HPLC injector loop (1 mL). The injector loop is connected to the optional column described in Paragraph 4.18. Rinse the centrifuge tube with 500 uL of hexane and add this rinsate to the injector loop. Load the combined concentrate and rinsate onto the column. Elute the column at 2 mL/min, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard the eluant. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is then discarded and 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through a new column to prepare it for the next sample.

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0-mL Reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of N_2. The final volume should be 100 uL for soil samples and 500 uL for sludge, still bottom, and fly ash samples; this is provided for guidance, the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted. Gently swirl the solvent on the lower portion of the vessel to ensure complete dissolution of the PCDD's and PCDF's.

9.10 Approximately 1 hr before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial (Paragraph 4.16). Add to this sufficient recovery standard ($^{13}C_{12}$1,2,3,4-TCDD) to give a concentration of 500 ng/mL. (Example: 36 uL aliquot of extract and 4 uL of recovery standard solution. Remember to adjust the final result to correct for this dilution. Inject an appropriate aliquot (1 or 2 uL) of the sample into the GC/MS instrument.

10.0 GC/MS ANALYSIS

10.1 When toluene is employed as the final solvent use of a bonded phase column from Paragraph 4.3.2 is recommended. Solvent exchange into tridecane is required for other liquid phases or nonbonded columns (CP-Sil-88).

NOTE: Chromatographic conditions must be adjusted to account for solvent boiling points.

10.2 Calculate response factors for standards relative to the internal standards, $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD (see Section 11). Add the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) to the samples prior to injection. The concentration of the recovery standard in the sample extract must be the same as that in the calibration standards used to measure the response factors.

10.3 Analyze samples with selected ion monitoring, using all of the ions listed in Table 2. It is recommended that the GC/MS run be divided into five selected ion monitoring sections, namely: (1) 243, 257,, 304, 306, 320, 322, 332, 334, 340, 356, 376 (TCDD's, TCDF's, $^{13}C_{12}$-labeled internal and recovery standards, PeCDD's, PeCDF's, HxCDE); (2) 277, 293, 306, 332, 338, 340, 342, 354, 356, 358, 410 (peCDD's, PeCDF's, HpCDE); (3) 311, 327, 340, 356, 372, 374, 376, 388, 390, 392, 446, (HxCDD's, HxCDF's, OCDE); (4) 345, 361, 374, 390, 406, 408, 410, 422, 424, 426, 480 (HpCDD's, HpCDF's, NCDE) and (5) 379, 395, 408, 424, 442, 444, 458, 460, 470, 472, 514 (OCDD, OCDF, $^{13}C_{12}$-OCDD, DCDE). Cycle time not to exceed 1 sec/descriptor. It is recommended that selected ion monitoring section 1 should be applied during the GC run to encompass the retention window (determined in Paragraph 6.3) of the first- and last-eluting tetra-chlorinated isomers. If a response is observed at m/z 340 or 356, then the GC/MS analysis must be repeated; selected ion monitoring section 2 should then be applied to encompass the retention window of the first- and last-eluting penta-chlorinated isomers. HxCDE, HpCDE, OCDE, NCDE, DCDE, are abbreviations for hexa-, hepta-, octa-, nona-, and decachlorinated diphenyl ether, respectively.

10.4 Identification criteria for PCDD's and PCDF's:

10.4.1 All of the characteristic ions, i.e. quantitation ion, confirmation ions, listed in Table 2 for each class of PCDD and PCDF, must be present in the reconstructed ion chromatogram. It is desirable that the M - COCl ion be monitored as an additional requirement. Detection limits will be based on quantitation ions within the molecules in cluster.

10.4.2 The maximum intensity of each of the specified characteristic ions must coincide within 2 scans or 2 sec.

10.4.3 The relative intensity of the selected, isotopic ions within the molecular ion cluster of a homologous series of PCDD's of PCDF's must lie within the range specified in Table 3.

10.4.4 The GC peaks assigned to a given homologous series must have retention times within the window established for that series by the column performance solution.

10.5 Quantitate the PCDD and PCDF peaks from the response relative to the appropriate internal standard. Recovery of each internal standard) vs. the recovery standard must be greater than 40 percent. It is recommended that samples with recoveries of less than 40 percent or greater than 120 percent be re-extracted and re-analyzed.

NOTE: These criteria are used to assess method performance; when properly applied, isotope dilution techniques are independent of internal standard recovery.

In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry or HRGC/MS/MS is suggested.

11.0 CALCULATIONS

NOTE: The relative response factors of a given congener within any homologous series are known to be different. However, for purposes of these calculations, it will be assumed that every congener within a given series has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, a 2,3,7,8-substituted isomer that is commercially available was chosen as representative of each series. All relative response factor calculations for a given homologous series are based on that compound.

11.1 Determine the concentration of individual isomers of tetra-, penta, and hexa-CDD/CDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 334) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 334 of $^{13}C_{12}$-2,3,7,8-TCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.1 Determine the concentration of individual isomers of hepta-CDD/CDF and the concentration of OCDD and OCDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-OCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 472) of the internal standard, $^{13}C_{12}$-OCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 472 of $^{13}C_{12}$-OCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.2 Relative response factors are calculated using data obtained from the analysis of multi-level calibration standards according to the equation:

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion of the appropriate internal standard (m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD; m/z 472 for $^{13}C_{12}$-OCDD).

C_{is} = concentration of the appropriate internal standard, $^{13}C_{12}$-2,3,7,8-TCDD or $^{13}C_{12}$-OCDD)

C_s = concentration of the compound of interest.

11.1.3 The concentrations of unknown isomers of TCDD shall be calculated using the mean RRF determined for 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDD or any available 2,3,7,8,X-PeCDD isomer.

The concentrations of unknown isomers of HxCDD shall be calculated using the mean RRF determined for 1,2,3,4,7,8-HxCDD or any available 2,3,7,8,-X,Y-HXCDD isomer.

The concentrations of unknown isomers of HpCDD shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDD or any available 2,3,7,8,X,Y,Z-HpCDD isomer.

The concentrations of unknown isomers of TCDF shall be calculated using the mean RRF determined for 2,3,7,8-TCDF.

The concentrations of unknown isomers of PeCDF shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDF or any available 2,3,7,8,X-PeCDF isomer.

The concentrations of unknown isomers of HxCDF shall be calculated using the mean RRF determined for 1,2,4,7,8-HxCDF or any available 2,3,7,8-X,Y-HxCDF isomer.

The concentrations of unknown isomers of HpCDF shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDF or any available 2,3,7,8,X,Y,Z-HpCDF isomer.

The concentration of the octa-CDD and octa-CDF shall be calculated using the mean RRF determined for each.

Mean relative response factors for selected PCDD's and PCDF's are given in Table 4.

11.1.4 Calculate the percent recovery, R_{is}, for each internal standard in the sample extract, using the equation:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times RF_r \times Q_{is}} \times 100\%$$

where:

A_{rs} = Area of quantitation ion (m/z 334) of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{rs} = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, added to extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of the multi-level calibration standards according to the equation:

$$RF_r = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

where:

C_{rs} = Concentration of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

11.1.5 Calculation of total concentration of all isomers within each homologous series of PCDD's and PCDF's.

Total concentration of PCDD's or PCDF's = Sum of the concentrations of the individual PCDD or PCDF isomers

11.4 Report results in nanograms per gram; when duplicate and spiked samples are reanalyzed, all data obtained should be reported.

11.5 Accuracy and Precision. Table 5 gives the precision data for revised Method 8280 for selected analytes in the matrices shown. Table 6 lists recovery data for the same analyses. Table 2 shows the linear range and variation of response factors for selected analyte standards. Table 8 provides the method detection limits as measured in specific sample matrices.

11.6 Method Detection Limit. The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The procedure used to determine the MDL values reported in Table 8 was obtained from Appendix A of EPA Test Methods manual, EPA-600/4-82-057 July 1982, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater."

11.7 Maximum Holding Time (MHT). Is that time at which a 10 percent change in the analyte concentration (C_{t10}) occurs and the precision of the method of measurement allows the 10 percent change to be statistically different from the 0 percent change (C_{t0}) at the 90 percent confidence level. When the precision of the method is not sufficient to statistically discriminate a 10 percent change in the concentration from 0 percent change, then the maximum holding time is that time where the percent change in the analyte concentration (C_{tn}) is statistically different than the concentration at 0 percent change (C_{t0}) and greater than 10 percent change at the 90 percent confidence level.

TABLE 1. REPRESENTATIVE GAS CHROMATOGRAPH RETENTION TIMES* OF ANALYTES

Analyte	50-m CP-Sil-88	30-m DB-5	3--m SP-2250
2,3,7,8-TCDF	25.2	17.8	26.7
2,3,7,8-TCDD	23.6	17.4	26.7
1,2,3,4-TCDD	24.1	17.3	26.5
1,2,3,4,7-PeCDD	30.0	20.1	28.1
1,2,3,4,7,8-HxCDD	39.5	22.1	30.6
1,2,3,4,6,7,8-HpCDD	57.0	24.1	33.7
OCDD	NM	25.6	NM

*Retention time in min, using temperature programs shown below.

NM = not measured.

Temperature Programs:

CP-Sil-88	60°C-190°C at 20°/min; 190°-240° at 5°/min.
DB-5 30 m x 0.25 mm Thin film (0.25 um)	170°, 10 min; then at 8°/min to 320°C, hold at 320°C 20 min (until OCDD elutes).
SP-2250	70°-320° at 10°/minute.

Column Manufacturers

CP-Sil-88	Chrompack, Incorporated, Bridgewater, New Jersey
DB-5,	J and W Scientific, Incorporated, Rancho Cordova, California
SP-2250	Supelco, Incorporated, Bellefonte, Pennsylvania

TABLE 2. IONS SPECIFIED[a] FOR SELECTED ION MONITORING FOR PCDD'S AND PCDF'S

	Quantitation ion	Confirmation ions	M-COCl
PCDD's			
$^{13}C_{12}$-Tetra	334	332	---
Tetra	322	320	257
Penta	356	354;358	293
Hexa	390	388;392	327
Hepta	424	422;426	361
Octa	460	458	395
$^{13}C_{12}$-Octa	472	470	
PCDF's			
Tetra	306	304	243
Penta	340	338;342	277
Hexa	374	372;376	311
Hepta	408	406;410	345
Octa	444	442	379

[a] Ions at m/z 376 (HxCDE), 410 (HpCDE), 446 (OCDE), 480 (NCDE) and 514 (DCDE) are also included in the scan monitoring sections (1) to (5), respectively. See Paragraph 10.3.

TABLE 3. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDD'S AND PCDF'S

	Selected ions (m/z)	Relative intensity
PCDD's		
Tetra	320/322	0.65-0.89
Penta	358/356	0.55-0.75
Hexa	392/390	0.69-0.93
Hepta	426/424	0.83-1.12
Octa	458/460	0.75-1.01
PCDF's		
Tetra	304/306	0.65-0.89
Penta	342/340	0.55-0.75
Hexa	376/374	0.69-0.93
Hepta	410/408	0.83-1.12
Octa	442/444	0.75-1.01

TABLE 4. MEAN RELATIVE RESPONSE FACTORS OF CALIBRATION STANDARDS

Analyte	RRF[a]	RSD% (n = 5)	Quantitation ion (m/z)
2,3,7,8-TCDD	1.13	3.9	322
1,2,3,7,8-PeCDD	0.70	10.1	356
1,2,3,4,7,8-HxCDD	0.51	6.6	390
1,2,3,4,6,7,8-HpCDD[b]	1.08	6.6	424
OCDD[b]	1.30	7.2	460
2,3,7,8-TCDF	1.70	8.0	306
1,2,3,7,8-PeCDF	1.25	8.7	340
1,2,3,4,7,8-HxCDF	0.84	9.4	374
1,2,3,4,6,7,8-HpCDF[b]	1.19	3.8	444
OCDF[b]	1.57	8.6	408
$^{13}C_{12}$-2,3,7,8-TCDD	1.00	-	334
$^{13}C_{12}$-1,2,3,4-TCDD	0.75	4.6	334
$^{13}C_{12}$-OCDD	1.00	-	472

---

[a] The RRF value is the mean of the five determinations made. Nominal weights injected were 0.2, 0.5, 1.0, 2.0 and 5.0 ng.

[b] RRF values for these analytes were determined relative to $^{13}C_{12}$-OCDD. All other RRF's were determined relative to $^{13}C_{12}$-2,3,7,8-TCDD.

Instrument Conditions/Tune - GC/MS system was tuned as specified in Paragraph 6.3. RRF data was acquired under SIM control, as specified in Paragraph 10.3.

GC Program - The GC column temperature was programmed as specified in Paragraph 4.3.2(b).

TABLE 5. PRECISION DATA FOR REVISED METHOD 8280

		Analyte level (ng/g)			
Compound	Matrix[a]	Native	Native + spike	N	Percent RSD
2,3,7,8-TCDD	clay	ND[b]	5.0	4	4.4
	soil	378	378	4	2.8
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom	487	487	4	24
1,2,3,4-TCDD	clay	ND	5.0	3	1.7
	soil	ND	25.0	4	1.1
	sludge	ND	125	4	9.0
	fly ash	38.5	38.5	4	7.9
	still bottom	ND	2500	4	-
1,3,6,8-TCDD	clay	ND	2.5	4	7.0
	soil	ND	25.0	4	5.1
	sludge	ND	125	4	3.1
	fly ash	19.1	19.1	2	-
	still bottom	227	2727	2	-
1,3,7,9-TCDD	clay	ND	2.5	4	19
	soil	ND	25.0	4	2.3
	sludge	ND	125.0	4	6.5
	fly ash	58.4	58.4	2	-
	still bottom	ND	2500	2	-
1,3,7,8-TCDD	clay	ND	5.0	4	7.3
	soil	ND	25.0	4	1.3
	sludge	ND	125	4	5.8
	fly ash	16.0	16.0	4	3.5
	still bottom	422	2920	2	-
1,2,7,8-TCDD	clay	ND	5.0	4	7.7
	soil	ND	25.0	4	9.0
	sludge	ND	125	4	7.7
	fly ash	2.6	2.6	3	23
	still bottom	ND	2500	2	-
1,2,8,9-TCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	0.6
	sludge	ND	125	4	1.9
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-

TABLE 5 (Continued)

		Analyte level (ng/g)			
Compound	Matrix[a]	Native	Native + spike	N	Percent RSD
1,2,3,4,7-PeCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	2.8
	sludge	ND	125	4	4.6
	fly ash	25.8	25.8	2	6.9
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDD	clay	ND	5.0	4	25
	soil	ND	25.0	4	20
	sludge	ND	125	4	4.7
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,7,8-HxCDD	clay	ND	5.0	4	38
	soil	ND	25.0	4	8.8
	sludge	ND	125	4	3.4
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	4	-
	soil	ND	25.0	4	-
	sludge[c]	8760	8780	4	-
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-
1,2,7,8-TCDF	clay	ND	5.0	4	3.9
	soil	ND	25.0	4	1.0
	sludge	ND	125	4	7.2
	fly ash	7.4	7.4	3	7.6
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDF	clay	ND	5.0	4	6.1
	soil	ND	25.0	4	5.0
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom[3]	25600	28100	2	-
1,2,3,4,7,8-HxCDF	clay	ND	5.0	4	26
	soil	ND	25.0	4	6.8
	sludge	13.6	139	4	5.6
	fly ash	24.2	24.2	4	13.5
	still bottom	ND	2500	2	-

TABLE 5. (Continued)

Compound	Analyte level (ng/g) Matrix[a]	Native	Native + spike	N	Percent RSD
OCDF	clay	ND	-	-	-
	soil	ND	-	-	-
	sludge	192	317	4	3.3
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-

[a] matrix types:

clay: pottery clay.

soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator; resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column only. (Carbon column not used.)

[b] ND - not detected at concentration injected (final volume 0.1 mL or greater).

[c] Estimated concentration out of calibration range of standards.

TABLE 6. RECOVERY DATA FOR REVISED METHOD 8280

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
2,3,7,8-TCDD	clay	ND	5.0	61.7
	soil	378	-	-
	sludge	ND	125	90.0
	fly ash	ND	46	90.0
	still bottom	487	-	-
1,2,3,4-TCDD	clay	ND	5.0	67.0
	soil	ND	25.0	60.3
	sludge	ND	125	73.1
	fly ash	38.5	46	105.6
	still bottom	ND	2500	93.8
1,3,6,8-TCDD	clay	ND	2.5	39.4
	soil	ND	25.0	64.0
	sludge	ND	125	64.5
	fly ash	19.1	46	127.5
	still bottom	227	2500	80.2
1,3,7,9-TCDD	clay	ND	2.5	68.5
	soil	ND	25.0	61.3
	sludge	ND	125	78.4
	fly ash	58.4	46	85.0
	still bottom	ND	2500	91.7
1,3,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	79.3
	sludge	ND	125	78.9
	fly ash	16.0	46	80.2
	still bottom	615	2500	90.5
1,2,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	75.3
	sludge	ND	125	80.4
	fly ash	2.6	46	90.4
	still bottom	ND	2500	88.4
1,2,8,9-TCDD	clay	ND	5.0	59.7
	soil	ND	25.0	60.3
	sludge	ND	125	72.8
	fly ash	ND	46	114.3
	still bottom	ND	2500	81.2

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7-PeCDD	clay	ND	5.0	58.4
	soil	ND	25.0	62.2
	sludge	ND	125	79.2
	fly ash	25.8	46	102.4
	still bottom	ND	2500	81.8
1,2,3,7,8-PeCDD	clay	ND	5.0	61.7
	soil	ND	25.0	68.4
	sludge	ND	125	81.5
	fly ash	ND	46	104.9
	still bottom	ND	2500	84.0
1,2,3,4,7,8-HxCDD	clay	ND	5.0	46.8
	soil	ND	25.0	65.0
	sludge	ND	125	81.9
	fly ash	ND	46	125.4
	still bottom	ND	2500	89.1
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	ND
	soil	ND	25.0	ND
	sludge[d]	8780	125	-
	fly ash	ND	-	-
	still bottom	ND	-	-
2,3,7,8-TCDD (C-13)	clay	ND	5.0	64.9
	soil	ND	25.0	78.8
	sludge	ND	125	78.6
	fly ash	ND	46	88.6
	still bottom	ND	2500	69.7
1,2,7,8-TCDF	clay	ND	5.0	65.4
	soil	ND	25.0	71.1
	sludge	ND	125	80.4
	fly ash	7.4	46	90.4
	still bottom	ND	2500	104.5
1,2,3,7,8-PeCDF	clay	ND	5.0	57.4
	soil	ND	25.0	64.4
	sludge	ND	125	84.8
	fly ash	ND	46	105.8
	still bottom	25600	2500	-

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7,8-HxCDF	clay	ND	5.0	54.2
	soil	ND	25.0	68.5
	sludge	13.6	125	82.2
	fly ash	24.2	46	91.0
	still bottom	ND	2500	92.9
OCDF	clay	ND	-	-
	soil	ND	-	-
	sludge	192	125	86.8
	fly ash	ND	-	-
	still bottom	ND	-	-

[a] matrix types:

clay: pottery clay.

soil: Times Beach, Missouri soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator: resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenol wastewaters.

The clay, soil and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[b] Final volume of concentrate 0.1 mL or greater, ND means below quantification limit, 2 or more samples analyzed.

[c] Amount of analyte added to sample, 2 or more samples analyzed.

[d] Estimated concentration out of calibration range of standards.

TABLE 7. LINEAR RANGE AND VARIATIOIN OF RESPONSE FACTORS

Analyte	Linear range tested (pg)	n[b]	Mean RF	%RSD
1,2,7,8-TCDF[a]	50-6000	8	1.634	12.0
2,3,7,8-TCDD[a]	50-7000	7	0.721	11.9
2,3,7,8-TCDF	300-4000	5	2.208	7.9

[a] Response factors for these analytes were calculated using 2,3,7,8-TCDF as the internal standard. The response factors for 2,3,7,8-TCDF were calculated vs. $^{13}C_{12}$-1,2,3,4-TCDD.

[b] Each value of n represents a different concentration level.

TABLE 8. METHOD DETECTION LIMITS OF $^{13}C_{12}$ - LABELED PCDD'S and PCDF'S IN REAGENT WATER (PPT) AND ENVIRONMENTAL SAMPLES (PPB)

$^{13}C_{12}$-Labeled Analyte	Reagent Water[a]	Missouri Soil[b]	Fly-Ash[b]	Industrial Sludge[c]	Still-Bottom[d]	Fuel Oil[d]	Fuel Oil/Sawdust[b]
2,3,7,8-TCDD	0.44	0.17	0.07	0.82	1.81	0.75	0.13
1,2,3,7,8-PeCDD	1.27	0.70	0.25	1.34	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	2.21	1.25	0.55	2.30	6.21	5.02	0.36
1,2,3,4,6,7,8-HpCDD	2.77	1.87	1.41	4.65	4.59	8.14	0.51
OCDD	3.93	2.35	2.27	6.44	10.1	23.2	1.48
2,3,7,8-TCDF	0.63	0.11	0.06	0.46	0.26	0.48	0.40
1,2,3,7,8-PeCDF	1.64	0.33	0.16	0.92	1.61	0.80	0.43
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	2.17	2.27	2.09	2.22

[a] Sample size 1,000 mL.
[b] Sample size 10 g.
[c] Sample size 2 g.
[d] Sample size 1 g.
Note: The final sample-extract volume was 100 uL for all samples.

Matrix types used in MDL Study:

- Reagent water: distilled, deionized laboratory water.
- Missouri soil: soil blended to form a homogeneous sample.
- Fly-ash: alkaline ash recovered from the electrostatic precipitator of a coal-burning power plant.
- Industrial sludge: sludge from cooling tower which received creosotic and pentachlorophenolic wastewaters. Sample was ca. 70 percent water, mixed with oil and sludge.
- Still-bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.
- Fuel oil: wood-preservative solution from the modified Thermal Process tanks. Sample was an oily liquid (>90 percent oil) containing no water.
- Fuel oil/Sawdust: sawdust was obtained as a very fine powder from the local lumber yard. Fuel oil (described above) was mixed at the - percent (w/w) level.

Procedure used for the Determination of Method Detection Limits was obtained from "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" Appendix A, EPA-600/4-82-057, July 1982. Using this procedure, the method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero.

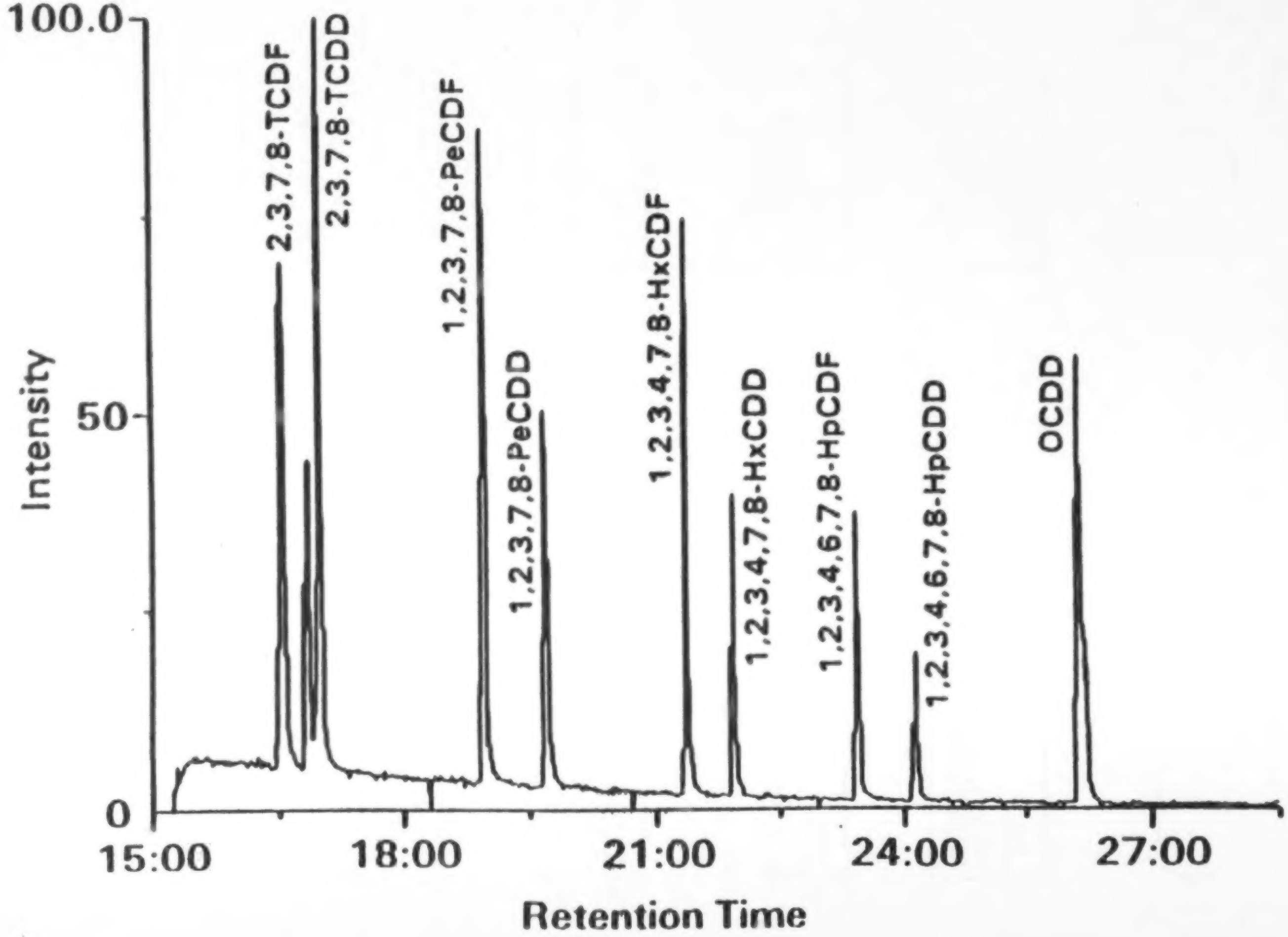
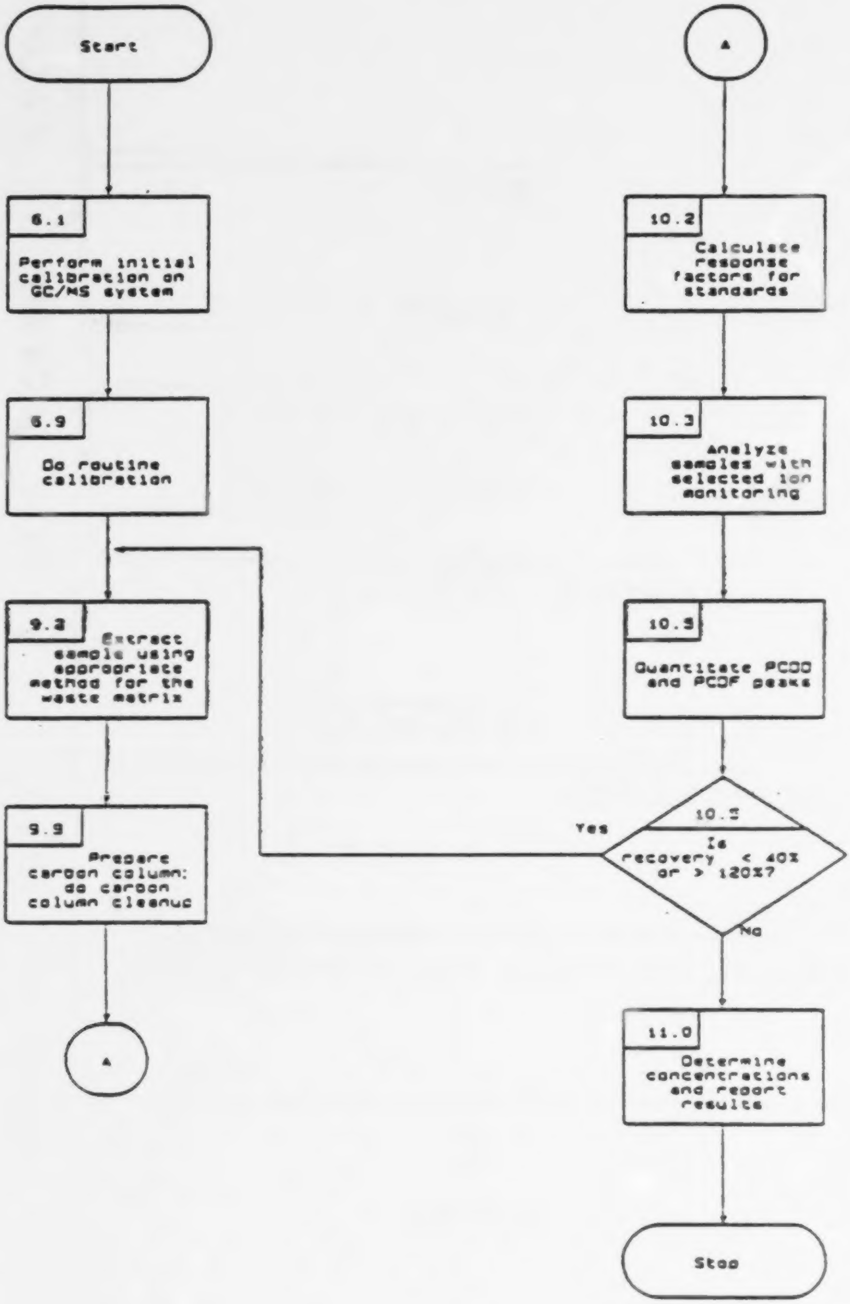


Figure 2. Mass Chromatogram of Selected PCDD and PCDF Congeners.

METHOD 8280

POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZONFURANS


Start
6.1
Perform initial calibration on GC/MS system
6.9
Do routine calibration
9.2
Extract sample using appropriate method for the waste matrix
9.3
Prepare carbon column; do carbon column cleanup
A
A
10.2
Calculate response factors for standards
10.3
Analyze samples with selected ion monitoring
10.5
Quantitate PCDD and PCDF peaks
10.5
Is recovery < 40% or > 120%?
Yes
No
11.0
Determine concentrations and report results
Stop

APPENDIX A

SIGNAL-TO-NOISE DETERMINATION METHODS

MANUAL DETERMINATION

This method corresponds to a manual determination of the S/N from a GC/MS signal, based on the measurement of its peak height relative to the baseline noise. The procedure is composed of four steps as outlined below. (Refer to Figure 1 for the following discussion).

1. Estimate the peak-to-peak noise (N) by tracing the two lines (E_1 and E_2) defining the noise envelope. The lines should pass through the estimated statistical mean of the positive and the negative peak excursions as shown in Figure 1. In addition, the signal offset (0) should be set high enough such that negative-going noise (except for spurious negative spikes) is recorded.
2. Draw the line (C) corresponding to the mean noise between the segments defining the noise envelope.
3. Measure the height of the GC/MS signal (S) at the apex of the peak relative to the mean noise C. For noisy GC/MS signals, the average peak height should be measured from the estimated mean apex signal D between E_3 and E_4.
4. Compute the S/N.

This method of S/N measurement is a conventional, accepted method of noise measurement in analytical chemistry.

INTERACTIVE COMPUTER GRAPHICAL METHOD

This method calls for the measurement of the GC/MS peak area using the computer data system and Eq. 1:

$$S/N = \frac{A/t}{\dfrac{A_l/2t + A_r/2t}{2}}$$

where t is the elution time window (time interval, t_2-t_2, at the base of the peak used to measure the peak area A). (Refer to Figure 2, for the following discussion).

A_l and A_r correspond to the areas of the noise level in a region to the left (A_l) and to the right (A_r) of the GC peak of interest.

The procedure to determine the S/N is as follows:

1. Estimate the average negative peak excursions of the noise (i.e., the low segment-E_2-of the noise envelope). Line E_2 should pass through the estimated statistical mean of the negative-going noise excursions. As stated earlier, it is important to have the signal offset (0) set high enough such that negative-going noise is recorded.

2. Using the cross-hairs of the video display terminal, measure the peak area (A) above a baseline corresponding to the mean negative noise value (E_2) and between the time t_1 and t_2 where the GC/MS peak intersects the baseline, E_2. Make note of the time width $t=t_2-t_1$.

3. Following a similar procedure as described above, measure the area of the noise in a region to the left (A_l) and to the right (A_r) of the GC/MS signal using a time window twice the size of t, that is, 2 x t.

The analyst must sound judgement in regard to the proper selection of interference-free regions in the measurement of A_l and A_r. It is not recommended to perform these noise measurements (A_l and A_r) in remote regions exceeding ten time widths (10t).

4. Compute the S/N using Eq. 1.

NOTE: If the noise does not occupy at least 10 percent of the vertical axis (i.e., the noise envelope cannot be defined accurately), then it is necessary to amplify the vertical axis so that the noise occupies 20 percent of the terminal display (see Figure 3).

FIGURE CAPTIONS

Figure 1. Manual determination of S/N.
The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E_1 and E_2, and between the apex average noise extremes, E_3 and E_4, at the apex of the signal. Note, it is imperative that the instrument's interface amplifier electronic's zero offset be set high enough such that negative-going baseline noise is recorded.

Figure 2. Interactive determination of S/N.
The peak area (A) is measured above the baseline average negative noise E_2 and between times t_1 and t_2. The noise is obtained from the areas A_l and A_r measured to the left and to the right of the peak of interest using time windows T_l and T_r ($T_l = T_r = 2t$).

Figure 3. Interactive determination of S/N.
A) Area measurements without amplification of the vertical axis. Note that the noise cannot be determined accurately by visual means. B) Area measurements after amplification (10X) of the vertical axis so that the noise level occupies approximately 20 percent of the display, thus enabling a better visual estimation of the baseline noise, E_1, E_2, and C.

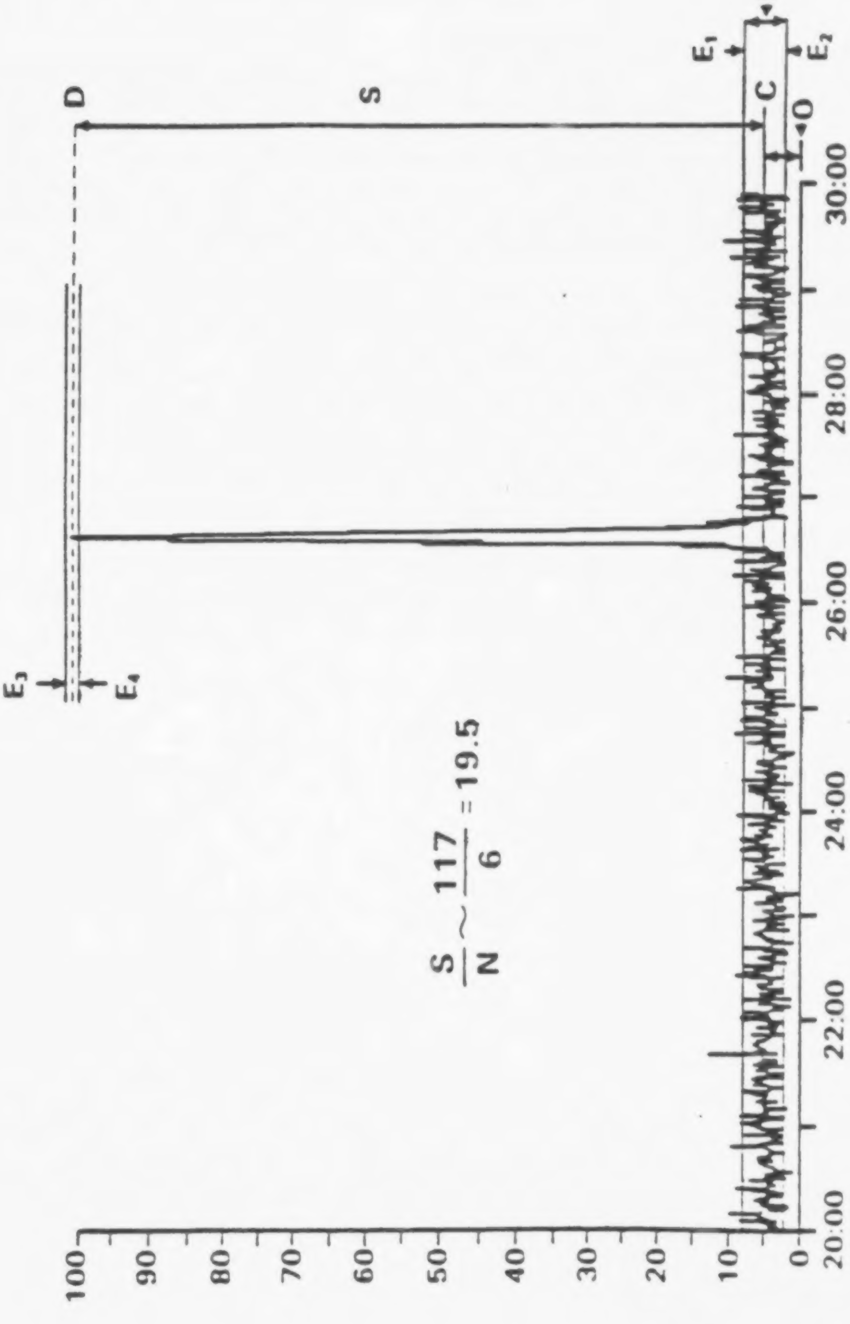


Figure 1. Manual Determination of S/N.

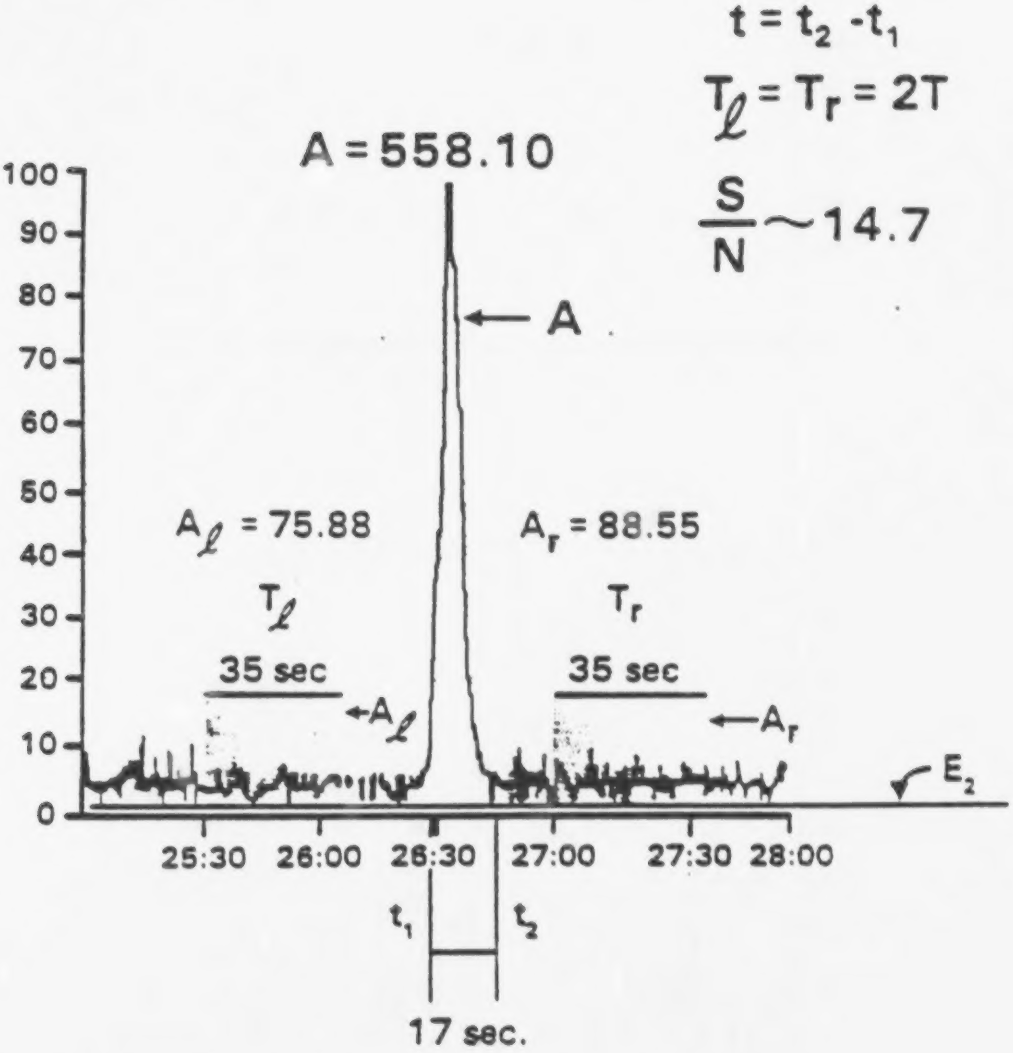


Figure 2. Interactive Determination of S/N.

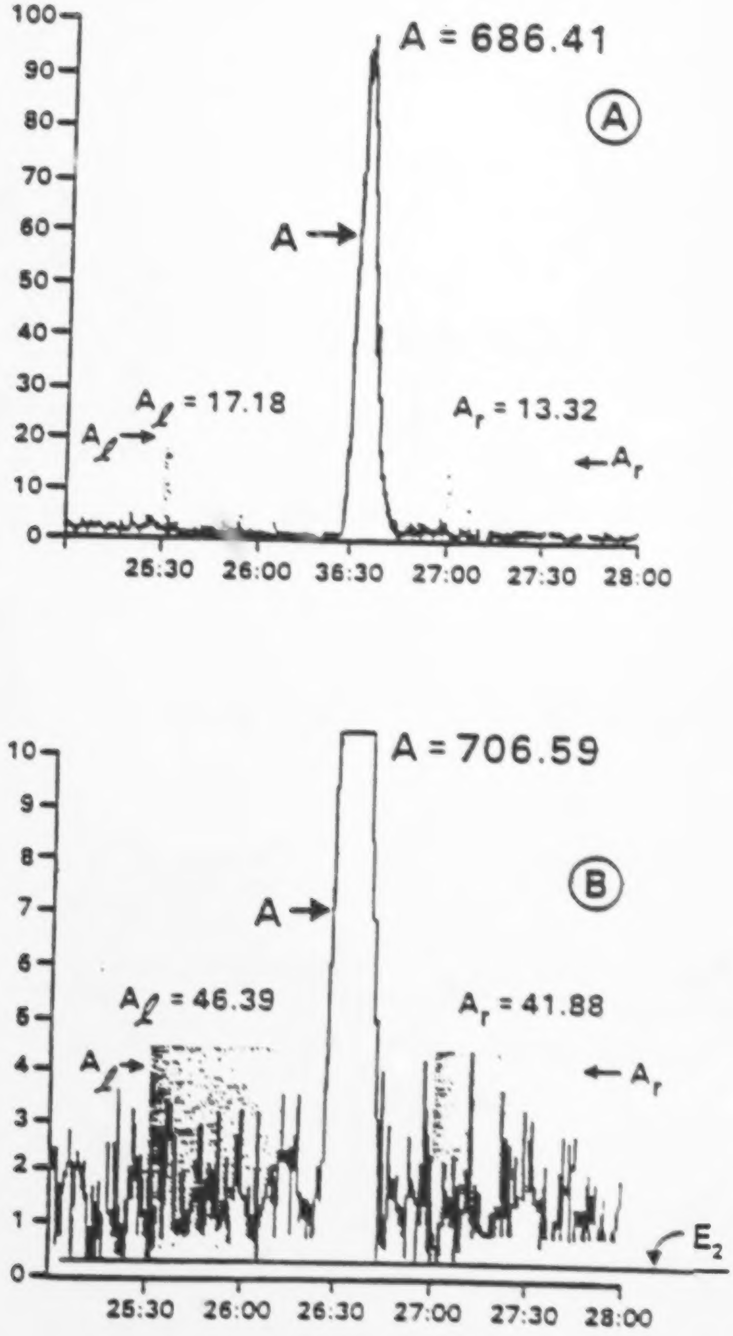


Figure 3. Interactive Determination of S/N.

APPENDIX B

RECOMMENDED SAFETY AND HANDLING PROCEDURES FOR PCDD'S/PCDF'S

1. The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in the course of laboratory animal studies. The 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in various organic solvents ranges from about 0.001 perent to 0.14 percent. The physical properties of the 135 other tetra- through octa-chlorinated PCDD/PCDF have not been well established, although it is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer. On the basis of the available toxicological and physical property data for TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories are required, and laboratory personel entering these laboratories should wear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, and when handling samples thought to be particularly hazardous, an additional set of gloves are also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are processed, removal of these from sample contaners, as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

3. All laboratory ware, safety clothing, and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-aproved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the laboratory. Typically, if the detectable level of TCDD or TCDF from such a test is greater than 50 ng/m^2, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is 500 ng/m^2. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scurbbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgeable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME ____________________ CONTRACT No. ____________________

CASE No. ____________________

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY ____________________________________

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME ____________________ CONTRACT No. ____________________

CASE No. ____________________

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME ____________________ CONTRACT No. ____________________

CASE No. ____________________

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY ____________________

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME ____________________ CONTRACT No. ____________________

CASE No. ____________________

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

DIOXIN RAW SAMPLE DATA FORM 8280-2

LAB NAME ____________ ANALYST(s) ____________ CASE No. ____________

SAMPLE No. ____________ TYPE OF SAMPLE ____________ CONTRACT No. ____________

SAMPLE SIZE ____________ % MOISTURE ____________ FINAL EXTRACT VOLUME ____________

EXTRACTION METHOD ____________ ALIQUOT USED FOR ANALYSIS ____________

CLEAN UP OPTION ____________

CONCENTRATION FACTOR ____________ DILUTION FACTOR ____________

DATE EXTRACTED ____________ DATA ANALYZED ____________

VOLUME $^{13}C_{12}$-1,2,3,4-TCDD ADDED ____________ TO SAMPLE VOLUME ____________

VOLUME INJECTED ____________ Wt $^{13}C_{12}$-1,2,3,4-TCDD ADDED ____________

Wt $^{13}C_{12}$-2,3,7,8-TCDD ADDED ____________ $^{13}C_{12}$-2,3,7,8-TCDD % RECOVERY ____________

Wt $^{13}C_{12}$-2,3,7,8-OCDD ADDED ____________ $^{13}C^{12}$-OCDD % RECOVERY ____________

$^{13}C_{12}$-2,3,7,8-TCDD RRF ____________ $^{13}C_{12}$-OCDD RRF ____________

$^{13}C_{12}$-2,3,7,8-TCDD

AREA 332 ____________ AREA 334 ____________ RATIO 332/334 ____________

$^{13}C_{12}$-OCDD AREA 470 ____________ AREA 472 ____________ RATIO 470/472 ____________

RT 2,3,7,8-TCDD (Standard) ____________ RT 2,3,7,8-TCDD (Sample) ____________

$^{13}C_{12}$-2,3,7,8-TCDD - $^{13}C_{12}$-1,2,3,4-TCDD Percent Valley ____________

DIOXIN INITIAL CALIBRATION STANDARD DATA SUMMARY

FORM 8280-3

CASE No. ____________________

Lab Name ____________________

Contract No. ____________________

Date of Initial Calibration ________

Analyst(s) ____________________

Relative to $^{13}C_{12}$-2,3,7,8-TCDD ____________ or $^{13}C_{12}$-1,2,3,4-TCDD ________

CALIBRATION STANDARD	RRF 1	RRF 2	RRF 3	RRF 4	RRF 5	MEAN	%RSD
TCDD							
PeCDD							
HxCDD							
HpCDD							
OCDD							
TCDF							
PeCDF							
HxCDF							
HpCDF							
OCDF							

FORM 8280-3 (Continued)

CONCENTRATIONS IN PG/UL

	1	2	3	4	5
TCDD					
PeCDD					
HxCDD					
HpCDD					
OCDD					
TCDF					
PeCDF					
HxCDF					
HpCDF					
OCDF					

DIOXIN CONTINUING CALIBRATION SUMMARY

FORM 8280-4

CASE No. ____________________

Lab Name ____________________

Contract No. ____________________

Date of Initial Calibration ________

Analyst(s) ____________________

Relative to $^{13}C_{12}$-2,3,7,8-TCDD ______

or $^{13}C_{12}$-1,2,3,4-TCDD ________

COMPOUND	$\overline{RRF}$	RRF	%D
TCDD			
PeCDD			
HxCDD			
HpCDD			
OCDD			
TCDF			
PeCDF			
HxCDF			
HpCDF			
OCDF			

DIOXIN RAW SAMPLE DATA FORM 8280-5-A

LAB NAME ______________ ANALYST(s) ____________ CASE No. ______________

CONTRACT No. __________________ SAMPLE No. ____________________

TCDD REQUIRED 320/322 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD ________ 1,2,3,4-TCDD _______ RRF ________

SCAN #	RRT	AREA 322	AREA 320	AREA 257	320/ 322	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD ____________________

TCDF REQUIRED 304/306 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD ________ 1,2,3,4-TCDD ________ RRF _______

SCAN #	RRT	AREA 306	AREA 304	AREA 243	304/ 306	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD ____________________

DIOXIN RAW SAMPLE DATA FORM 8280-5-8

LAB NAME ______________ ANALYST(s) ____________ CASE No. ______________

CONTRACT No. __________________ SAMPLE No. ____________________

PeCDD REQUIRED 320/322 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _________ 1,2,3,4-TCDD _______ RRF ________

SCAN #	RRT	AREA 356	AREA 358	AREA 354	AREA 293	358/ 356	CONFIRM AS PeCDD Y/N	CONC.

TOTAL PeCDD ________________

PeCDF REQUIRED 342/340 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _________ 1,2,3,4-TCDD ________ RRF _______

SCAN #	RRT	AREA 340	AREA 342	AREA 338	AREA 277	342/ 340	CONFIRM AS PeCDF Y/N	CONC.

TOTAL PeCDF ____________________

DIOXIN RAW SAMPLE DATA FORM 8280-5-C

LAB NAME ______________ ANALYST(s) ____________ CASE No.______________

CONTRACT No.__________________ SAMPLE No.____________________

HxCDD REQUIRED 392/390 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD ________ 1,2,3,4-TCDD ______ RRF ________

SCAN #	RRT	AREA 390	AREA 392	AREA 388	AREA 327	392/ 390	CONFIRM AS HxCDD Y/N	CONC.

TOTAL HxCDD ____________________

HxCDF REQUIRED 376/374 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _________ 1,2,3,4-TCDD ________ RRF _______

SCAN #	RRT	AREA 376	AREA 374	AREA 372	AREA 311	376/ 374	CONFIRM AS HxCDF Y/N	CONC.

TOTAL HxCDF ____________________

DIOXIN RAW SAMPLE DATA FORM 8280-5-D

LAB NAME ______________ ANALYST(s) ___________ CASE No.______________

CONTRACT No.__________________ SAMPLE No.____________________

HpCDD REQUIRED 426/444 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD ________ 1,2,3,4-TCDD ______ RRF ________

SCAN #	RRT	AREA 424	AREA 426	AREA 422	AREA 361	426/ 424	CONFIRM AS HpCDD Y/N	CONC.

TOTAL HpCDD ____________________

HpCDF REQUIRED 410/408 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD __________ 1,2,3,4-TCDD ________ RRF ______

SCAN #	RRT	AREA 408	AREA 410	AREA 406	AREA 345	410/ 408	CONFIRM AS HpCDF Y/N	CONC.

TOTAL HpCDF ____________________

DIOXIN RAW SAMPLE DATA FORM 8280-5-E

LAB NAME ______________ ANALYST(s) ____________ CASE No.______________

CONTRACT No. __________________ SAMPLE No. ______________

OCDD REQUIRED 458/460 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD ________ 1,2,3,4-TCDD ______ RRF ________

SCAN #	RRT	AREA 460	AREA 458	AREA 395	458/ 460	CONFIRM AS OCDD Y/N	CONC.

TOTAL OCDD ____________________

OCDF REQUIRED 442/444 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD ________ 1,2,3,4-TCDD ________ RRF ______

SCAN #	RRT	AREA 444	AREA 442	AREA 379	442/ 444	CONFIRM AS OCDF Y/N	CONC.

TOTAL OCDF ____________________

DIOXIN SYSTEM PERFORMANCE CHECK ANALYSIS FORM 8280-6

LAB NAME ______________________ CASE No. ______________

BEGINNING DATE __________ TIME ____________ CONTRACT No. ________

ENDING DATE __________ TIME ____________ ANALYST(s) ________

PC SOLUTION IDENTIFIER ______________________________

ISOTOPIC RATIO CRITERIA MEASUREMENT

PCDD's	IONS RATIOED	RATIO AT BEGINNING OF 12 HOUR PERIOD	RATIO AT END OF 12 HOUR PERIOD	ACCEPTABLE WINDOW
Tetra	320/322			0.65-0.89
Penta	358/356			0.55-0.75
Hexa	392/390			0.69-0.93
Hepta	426/424			0.83-1.12
Octa	458/460			0.75-1.01
PCDF's				
Tetra	304/306			0.65-0.89
Penta	342-340			0.55-0.75
Hexa	376-374			0.69-0.93
Hepta	410/408			0.83-1.12
Octa	442/444			0.75-1.01

Ratios out of criteria

	Beginning	End
PCDD	_______ out of _______	_______ out of _______
PCDF	_______ out of _______	_______ out of _______

NOTE: One form is required for each 12 hour period samples are analyzed.

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

Wastes. Volume 1. EPA Contract 68–03–2552. January. 1981.

(20) National Research Council (NRC). Drinking Water and Health. Vol. 4. Safe Drinking Water Committee. National Academy Press. Washington, D.C. 1982.

(21) Office of Management and Budget (OMB). Interim Regulatory Impact Analyses Guidance. Washington D.C. June. 1981.

(22) Research Triangle Institute (RTI). Regulatory Impact Analysis for Expansion of Toxicity Characteristic Under RCRA. U.S. EPA Contract 68–01–7073. October. 1985.

(23) S-Cubed. Precision Evaluation of the TCLP Protocol For Non-Volatile Components. Draft Report. U.S. EPA Contract 68–03–1958. January 1986.

(24) Spellenberg, S.P. Organic Extraction Procedure. U.S. EPA Contract 68–01–6149. January. 1982.

(25) Technology Applications Inc. (TAI). Statistical Analysis of TCLP Development Data. U.S. EPA Contract 68–01–6938. May 28. 1985.

(26) U.S. EPA. Background Document. Section 261.24. Characteristic of Extraction Procedure Toxicity. National Technical Information Service (NTIS) PB 81–185–027. Springfield, Virginia. May. 1980.

(27) U.S. EPA. Test Methods for Evaluating Solid Wastes—Physical/Chemical Methods. Second ed. Government Printing Office (GPO) 055–002–81001–2. EPA SW–846. Washington, D.C. 1982.

(28) U.S. EPA. Guidelines for Performing Regulatory Impact Analysis. Washington, D.C. December. 1983.

(29) U.S. EPA Science Advisory Board (SAB). Report on the Review of EP–III. Washington, D.C. May. 1984.

(30) U.S. EPA. Background Document: Issues Relating to the Development and Use of Reference Doses to Support 40 CFR Part 268, Land Disposal Restrictions. Washington, D.C. November. 1985.

(31) U.S. EPA. Acceptable Daily Intake Workgroup Paper: Assessing Risks Associated With Systemic Toxicants. Washington, D.C. 1985.

(32) U.S. EPA. Verified Reference Doses (RfD's) of the U.S. EPA. Washington, D.C. 1985.

(33) U.S. EPA. Background Document For Toxicity Characteristic Leaching Procedure. Washington, D.C. February. 1986.

List of Subjects in 40 CFR Parts 261, 271, and 302

Administrative practice and procedure. Air pollution control. Chemicals. Confidential business information. Hazardous materials. Hazardous materials transportation. Hazardous substances. Hazardous waste. Indian lands. Intergovernmental relations. Natural resources. Nuclear materials. Penalties. Pesticides and pests. Radioactive materials. Recycling. Reporting and recordkeeping requirements. Superfund. Water pollution control. Water supply. Waste treatment and disposal.

Dated: May 31, 1986.

Lee M. Thomas,

Administrator.

For the reasons set out in the preamble, it is proposed to amend Title 40 of the Code of Federal Regulations as follows:

PART 261—IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

1. The authority citation for Part 261 continues to read as follows:

Authority: Secs. 1006, 2002(a), 3001, and 3002 of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976, as amended (42 U.S.C. 6905, 6912(a), 6921, and 6922).

2. § 261.24 is revised to read as follows:

§ 261.24 Toxicity characteristic.

(a) A solid waste exhibits the characteristic of toxicity if, using the test methods described in Appendix II or equivalent methods approved by the Administrator under the procedures set forth in §§ 260.20 and 260.21, the extract from a representative sample of the waste contains any of the contaminants listed in Table 1 at the concentration equal to or greater than the respective value given in that Table. Where the waste contains less than 0.5 percent filterable solids, the waste itself, after filtering using the methodology outlined in Appendix II, is considered to be the extract for the purpose of this section.

(b) A solid waste that exhibits the characteristic of toxicity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number specified in Table 1 which corresponds to the toxic contaminant causing it to be hazardous.

TABLE 1.—TOXICITY CHARACTERISTIC CONTAMINANTS AND REGULATORY LEVELS

HWNO and contaminant	CASNO	Regulatory level (mg/l)
D018—Acrylonitrile	107-13-1	5.0
D004—Arsenic	7440-38-2	5.0
D005—Barium	7440-39-3	100
D019—Benzene	71-43-2	0.07
D020—Bis(2-chloroethyl) ether	111-44-4	0.05
D006—Cadmium	7440-43-9	1.0
D021—Carbon disulfide	75-15-0	14.4
D022—Carbon tetrachloride	56-23-5	0.07
D023—Chlordane	57-74-9	0.03
D024—Chlorobenzene	108-90-7	1.4
D025—Chloroform	67-66-3	0.07
D007—Chromium	1333-82-0	5.0
D026—o-Cresol *	95-48-7	10.0
D027—m-Cresol *	108-39-4	10.0
D028—p-Cresol *	106-44-5	10.0
D016—2,4-D	94-75-7	1.4
D029—1,2-Dichlorobenzene	95-50-1	4.3
D030—1,4-Dichlorobenzene	106-46-7	10.8
D031—1,2-Dichloroethane	107-06-2	0.40
D032—1,1-Dichloroethylene	75-35-4	0.1
D033—2,4-Dinitrotoluene	121-14-2	0.13
D012—Endrin	72-20-8	0.003
D034—Heptachlor (and its hydroxide)	76-44-8	0.001
D035—Hexachlorobenzene	118-74-1	0.13

TABLE 1.—TOXICITY CHARACTERISTIC CONTAMINANTS AND REGULATORY LEVELS—Continued

HWNO and contaminant	CASNO	Regulatory level (mg/l)
D036—Hexachlorobutadiene	87-68-3	0.72
D037—Hexachloroethane	67-72-1	4.3
D038—Isobutanol	78-83-1	36
D008—Lead	7439-92-1	5.0
D013—Lindane	58-89-9	0.06
D009—Mercury	7439-97-6	0.2
D014—Methoxychlor	72-43-5	1.4
D039—Methylene chloride	75-09-2	8.6
D040—Methyl ethyl ketone	78-93-3	7.2
D041—Nitrobenzene	98-95-3	0.13
D042—Pentachlorophenol	87-86-5	3.6
D043—Phenol	108-95-2	14.4
D044—Pyridine	110-86-1	5.0
D010—Selenium	7782-49-2	1.0
D011—Silver	7440-22-4	5.0
D045—1,1,1,2-Tetrachloroethane	630-20-6	10.0
D046—1,1,2,2-Tetrachloroethane	79-34-5	1.3
D047—Tetrachloroethylene	127-18-4	0.1
D048—2,3,4,6-Tetrachlorophenol	58-90-2	1.5
D049—Toluene	108-88-3	14.4
D015—Toxaphene	8001-35-2	0.07
D050—1,1,1-Trichloroethane	71-55-6	30
D051—1,1,2-Trichloroethane	79-00-5	1.2
D052—Trichloroethylene	79-01-6	0.07
D053—2,4,5-Trichlorophenol	95-95-4	5.8
D054—2,4,6-Trichlorophenol	88-06-2	0.30
D017—2,4,5-TP (Silvex)	93-76-5	0.14
D055—Vinyl chloride	75-01-4	0.05

* o-, m-, and p-Cresol concentrations are added together and compared to a threshold of 10.0 mg/l.

3. Appendix II of Part 261 is revised to read as follows:

Appendix II—Toxicity Characteristic Leaching Procedure (TCLP)

1.0 *Scope and application.*

1.1 The TCLP is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual contaminants are not present in the waste, or that they are present, but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

2.0 *Summary of method* (See Figure 1).

2.1 For wastes containing less than 0.5% solids, the waste, after filtration through a 0.6–0.8 μm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than 0.5% solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis. The particle size of the solid phase is reduced (if necessary), weighed, and extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatiles (See Table 1). Following extraction, the liquid extract is separated from the solid phase by 0.6–0.8 μm glass fiber filter filtration.

2.3 If compatible (e.g. precipitate or multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the

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results are mathematically combined to yield volume weighted average concentration.

3.0 *Interferences.*

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 *Apparatus and materials.*

4.1 Agitation Apparatus: An acceptable agitation apparatus is one which is capable of rotating the extraction vessel in an end-over-end fashion (See Figure 2) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction vessel:

4.2.1 Zero-Headspace Extraction Vessel (ZHE). When the waste is a being tested for mobility of any volatile contaminants (See Table 1), an extraction vessel which allows for liquid/solid separation within the device, and which effectively precludes headspace (as depicted in Figure 3), is used. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without having to open the vessel (See Section 4.3.1). These vessels shall have an internal volume of 500 to 600 ml and be equipped to accommodate a 90 mm filter. Suitable ZHE devices known to EPA are identified in Table 3. These devices contain viton O-rings which should be replaced frequently.

4.2.2 When the waste is being evaluated for other than volatile contaminants, an extraction vessel which does not preclude headspace (e.g., 2-liter bottle) is used. Suitable extraction vessels include bottles made from various materials, depending on the contaminants to be analyzed and the nature of the waste (See Section 4.3.3). These bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid-solid separation and final extract filtration.

4.3 Filtration devices:

4.3.1 Zero-Headspace Extractor Vessel (See Figure 3): When the waste is being evaluated for volatiles, the zero-headspace extraction vessel is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter, and be able to withstand the pressure needed to accomplish separation (50 psi).

Note. When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the extract.

4.3.2 Filter Holder. When the waste is being evaluated for other than volatile compounds, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation is used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressure up to 50 psi and more. The type of filter holder used depends on the properties of the material to be filtered (See Section 4.3.3). These devices shall have a minimum internal volume of 300 ml and be equipped to accommodate a minimum filter size of 47 mm. Filter holders known to EPA to be suitable for use are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene, or polyvinyl chloride may be used when evaluating the mobility of metals.

4.4 Filters: Filters shall be made of borosilicate glass fiber, contain no binder materials, and have an effective pore size of 0.6–0.8 um, or equivalent. Filters known to EPA to meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid washed prior to use by rinsing with 1.0 N nitric acid followed by three consecutive rinses with deionized distilled water (minimum of 500 ml per rinse). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: Any of the commonly available pH meters are acceptable.

4.6 ZHE extract collection devices: TEDLAR* bags or glass, stainless steel or PTFE gas tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device.

4.7 ZHE extraction fluid collection devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a constant displacement pump, a gas tight syringe, pressure filtration unit (See Section 4.3.2), or another ZHE device).

4.8 Laboratory balance: Any laboratory balance accurate to within ±0.01 grams may be used (all weight measurements are to be within ±0.1 grams).

5.0 *Reagents.*

5.1 Water: ASTM Type 1 deionized, carbon treated, decarbonized, filtered water (or equivalent water that is treated to remove volatile components) shall be used when evaluating wastes for volatile contaminants. Otherwise, ASTM Type 2 deionized distilled water (or equivalent) is used. These waters should be monitored periodically for impurities.

5.2 1.0 N Hydrochloric acid (HCl) made from ACS Reagent grade.

5.3 1.0 N Nitric acid (HNO_3) made from ACS Reagent grade.

5.4 1.0 N Sodium hydroxide (NaOH) made from ACS Reagent grade.

5.5 Glacial acetic acid (HOAc) made from ACS Reagent grade.

5.6 Extraction fluid:

5.6.1 Extraction fluid #1: This fluid is made by adding 5.7 ml glacial HOAc to 500 ml of the appropriate water (See Section 5.1), adding 64.3 ml of 1.0 N NaOH, and diluting to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.

5.6.2 Extraction fluid #2: This fluid is made by diluting 5.7 ml glacial HOAc with ASTM Type 2 water (See Section 5.1) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

Note.—These extraction fluids shall be made up fresh daily. The pH should be checked prior to use to insure that they are made up accurately, and these fluids should be monitored frequently for impurities.

5.7 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 *Sample Collection, preservation, and handling.*

6.1 All samples shall be collected using a sampling plan that addresses the consideration discussed in "Test Methods for Evaluating Solid Wastes" (SW–846).

6.2 Preservatives shall not be added to samples.

6.3 Samples can be refrigerated unless it results in irreversible physical changes to the waste.

6.4 When the waste is to be evaluated for volatile contaminants, care must be taken to insure that these are not lost. Samples shall be taken and stored in a manner which prevents the loss of volatile contaminants. If possible, any necessary particle size reduction should be conducted as the sample is being taken (See Step 8.5). Refer to SW–846 for additional sampling and storage requirements when volatiles are contaminants of concern.

6.5 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. If they need to be stored, even for a short period of time, storage shall be at 4°C and samples for volatiles analysis shall not be allowed to come into contact with the atmosphere (i.e., no headspace).

7.0 *Procedure when volatiles are not involved.*

Although a minimum sample size of 100 grams is required, a larger sample size may be necessary, depending on the percent solids of the waste sample. Enough waste sample should be collected such that at least 75 grams of the solid phase of the waste (as determined using glass fiber filter filtration), is extracted. This will insure that there is adequate extract for the required analyses (e.g., semivolatiles, metals, pesticides and herbicides).

The determination of which extraction fluid to use (See Step 7.12) may also be conducted at the start of this procedure. This determination shall be on the solid phase of the waste (as obtained using glass fiber filter filtration).

7.1 If the waste will obviously yield no free liquid when subjected to pressure filtration, weigh out a representative subsample of the waste (100 gram minimum) and proceed to Step 7.11.

7.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device discussed in Section 4.3.2, and is outlined in Steps 7.3 to 7.9.

7.3 Pre-weigh the filter and the container which will receive the filtrate.

7.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (See Section 4.4).

7.5 Weigh out a representative subsample of the waste (100 gram minimum) and record weight.

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*TEDLAR is a registered trademark of DuPont.

7.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.7 Transfer the waste sample to the filter holder.

Note.—If waste material has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.5, to determine the weight of the waste sample which will be filtered.

Gradually apply vacuum or gentle pressure of 1–10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., does not result in any additional filtrate within any 2 minute period), filtration is stopped.

Note.—Instantaneous application of high pressure can degrade the glass fiber filter, and may cause premature plugging.

7.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note.—Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid—but even after applying vacuum or pressure filtration, as outlined in Step 7.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid.

7.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (See Step 7.3) from the total weight of the filtrate-filled container. The liquid phase may now be either analyzed (See Step 7.15) or stored at 4°C until time of analysis. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Step 7.5 or 7.7. Record the weight of the liquid and solid phases.

Note.—If the weight of the solid phase of the waste is less than 75 grams, review Step 7.0.

7.10 The sample will be handled differently from this point, depending on whether it contains more or less than 0.5% solids. If the sample obviously has greater than 0.5% solids go to Step 7.11. If it appears that the solid may comprise less than 0.5% of the total waste, the percent solids will be determined as follows:

7.10.1 Remove the solid phase and filter from the filtration apparatus.

7.10.2 Dry the filter and solid phase at 100±20°C until two successive weighings yield the same value. Record final weight.

7.10.3 Calculate the percent solids as follows:

Weight of dry waste and filters minus tared weight of filters divided by initial weight of waste (Step 7.5 or 7.7) multiplied by 100 equals percent solids.

7.10.4 If the solid comprises less than 0.5% of the waste, the solid is discarded and the liquid phase is defined as the TCLP extract. Proceed to Step 7.14.

7.10.5 If the solid is greater than or equal to 0.5% of the waste, return to Step 7.1, and begin the procedure with a new sample of waste. Do not extract the solid that has been dried.

Note.—This step is only used to determine whether the solid must be extracted, or whether it may be discarded unextracted. It is not used in calculating the amount of extraction fluid to use in extracting the waste, nor is the dried solid derived from this step subjected to extraction. A new sample will have to be prepared for extraction.

7.11 If the sample has more than 0.5% solids, it is now evaluated for particle size. If the solid material has a surface area per gram of material equal to or greater than 3.1 cm², or is capable of passing through a 9.5 mm (0.375 inch) standard sieve, proceed to Step 7.12. If the surface area is smaller or the particle size is larger than that described above, the solid material is prepared for extraction by crushing, cutting, or grinding the solid material to a surface area or particle size as described above. When surface area or particle size has been appropriately altered, proceed to Step 7.12.

7.12 This step describes the determination of the appropriate extracting fluid to use (See Sections 5.0 and 7.0).

7.12.1 Weigh out a small sub-sample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer a 5.0 gram portion to a 500 ml beaker or erlenmeyer flask.

7.12.2 Add 96.5 ml distilled deionized water (ASTM Type 2), cover with watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is < 5.0, extraction fluid #1 is used. Proceed to Step 7.13.

7.12.3 If the pH from Step 7.12.2 is >5.0, add 3.5 ml 1.0 N HCl, slurry for 30 seconds, cover with a watchglass, heat to 50°C, and hold for 10 minutes.

7.12.4 Let the solution cool to room temperature and record pH. If pH is <5.0, use extraction fluid #1. If the pH is >5.0, extraction fluid #2 is used.

7.13 Calculate the weight of the remaining solid material by subtracting the weight of the sub-sample taken for Step 7.12 from the original amount of solid material, as obtained from Step 7.1 or 7.9. Transfer remaining solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase.

Note.—If any of the solid phase remains adhered to the walls of the filter holder, or the container used to transfer the waste, its weight shall be determined, subtracted from the weight of the solid phase of the waste, as determined above, and this weight is used in calculating the amount of extraction fluid to add into the extractor bottle.

Slowly add an amount of the appropriate extraction fluid (See Step 7.12), into the extractor bottle equal to 20 times the weight of the solid phase that has been placed into the extractor bottle. Close extractor bottle tightly, secure in rotary extractor device and rotate at 30 ± 2 rpm for 18 hours. The temperature shall be maintained at 22 ± 3 °C during the extraction period.

Note.—As agitation continues, pressure may build up within the extractor bottle (due to the evolution of gasses such as carbon dioxide). To relieve these pressures, the extractor bottle may be periodically opened and vented into a hood.

7.14 Following the 18 hour extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new glass fiber filter as outlined in Step 7.7. This new filter shall be acid washed (See Section 4.4) if evaluating the mobility of metals.

7.15 The TCLP extract is now prepared as follows:

7.15.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 7.14 is defined as the TCLP extract. Proceed to Step 7.16.

7.15.2 If compatible (e.g., will not form precipitate or multiple phases), the filtered liquid resulting from Step 7.14 is combined with the initial liquid phase of the waste as obtained in Step 7.9. This combined liquid is defined as the TCLP extract. Proceed to Step 7.16.

7.15.3 If the initial liquid phase of the waste, as obtained from Step 7.9, is not or may not be compatible with the filtered liquid resulting from Step 7.14, these liquids are not combined. These liquids are collectively defined as the TCLP extract, are analyzed separately, and the results are combined mathematically. Proceed to Step 7.16.

7.16 The TCLP extract will be prepared and analyzed according to the appropriate SW–846 analytical methods identified in Appendix III of 40 CFR 261. TCLP extracts to be analyzed for metals shall be acid digested. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to 0.1 ml), conduct the appropriate analyses, and combine the results mathematically by using a simple weighted average:

$$\text{Final contaminant concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (l)
C_1 = The concentration of the contaminant of concern in the first phase (mg/l)
V_2 = The volume of the second phase (l)
C_2 = The concentration of the contaminant of concern in the second phase (mg/l)

7.17 The contaminant concentrations in the TCLP extract are compared to the thresholds identified in the appropriate regulations. Refer to Section 9 for quality assurance requirements.

8.0 *Procedure when volatiles are involved.*

The ZHE device has approximately a 500 ml internal capacity. Although a minimum sample size of 100 grams was required in the Section 7 procedure, the ZHE can only accommodate a maximum 100 percent solids sample of 25 grams, due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase. Step 8.4 provides the means of which to determine the approximate sample size for the ZHE device.

Although the following procedure allows for particle size reduction during the conduct of the procedure, this could result in the loss of volatile compounds. If possible, any necessary particle size reduction (See Step 8.5) should be conducted on the sample as it is being taken. Particle size reduction should only be conducted during the procedure if there is no other choice.

In carrying out the following steps, do not allow the waste to be exposed to the atmosphere for any more time than is absolutely necessary.

8.1 Pre-weigh the (evacuated) container which will receive the filtrate (See Section 4.6), and set aside.

8.2 Place the ZHE piston within the body of the ZHE (it may be helpful to first moisten the piston O-rings slightly with extraction fluid). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

8.3 If the waste will obviously yield no free liquid when subjected to pressure filtration, weigh out a representative subsample of the waste (25 gram maximum—See Step 8.0), record weight, and proceed to Step 8.5.

8.4 This step provides the means by which to determine the approximate sample size for the ZHE device. If the waste is liquid or multiphasic, follow the procedure outlined in Steps 7.2 to 7.9 (using the Section 7 filtration apparatus), and obtain the percent solids by dividing the weight of the solid phase of the waste by the original sample size used. If the waste obviously contains greater than 0.5% solids, go to Step 8.4.2. If it appears that the solid may comprise less than 0.5% of the waste, go to Step 8.4.1.

8.4.1 Determine the percent solids by using the procedure outlined in Step 7.10. If the waste contains less than 0.5% solids, weigh out a new 100 gram minimum representative sample, proceed to Step 8.7, and follow until the liquid phase of the waste is filtered using the ZHE device (Step 8.8). This liquid filtrate is defined as the TCLP extract, and is analyzed directly. If the waste contains greater than or equal to 0.5% solids, repeat Step 8.4 using a new 100 gram minimum sample, determine the percent solids, and proceed to Step 8.4.2.

8.4.2 If the sample is < 25% solids, weigh out a new 100 gram minimum representative sample, and proceed to Step 8.5. If the sample is > 25% solids, the maximum amount of sample the ZHE can accommodate is determined by dividing 25 grams by the percent solids obtained from Step 8.4. Weigh out a new representative sample of the determined size.

8.5 After a representative sample of the waste (sample size determined from Step 8.4) has been weighed out and recorded, the sample is now evaluated for particle size (See Step 8.0). If the solid material within the waste obviously has a surface area per gram of material equal to or greater than 3.1 cm^2, or is capable of passing through a 9.5 mm (0.375 inch) standard sieve, proceed immediately to Step 8.6. If the surface area is smaller or the particle size is larger than that described above, the solid material which does not meet the above criteria is separated from the liquid phase by sieving (or equivalent means), and the solid is prepared for extraction by crushing, cutting, or grinding to a surface area or particle size as described above.

Note.—Wastes and appropriate equipment should be refrigerated, if possible, to 4°C prior to particle size reduction. Grinding and milling machinery which generates heat shall not be used for particle size reduction. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

When surface area or particle size has been appropriately altered, the solid is recombined with the rest of the waste.

8.6 Waste slurries need not be allowed to stand to permit the solid phase to settle. Wastes that settle slowly shall not be centrifuged prior to filtration.

8.7 Transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

Note.—If waste material has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 8.4, to determine the weight of the waste sample which will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange), and with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1–10 psi (or more if necessary) to slowly force all headspace out of the ZHE device. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure.

8.8 Attach evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open valve. Begin applying gentle pressure of 1–10 psi to force the liquid phase into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within any 2 minute period, filtration is stopped. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect the filtrate collection container.

Note.—Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

8.9 The material in the ZHE is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note.—Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid—but even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the TCLP extraction as a solid.

If the original waste contained less than 0.5% solids, (See Step 8.4) this filtrate is defined as the TCLP extract; and is analyzed directly—proceed to Step 8.13.

8.10 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (See Step 8.1) from the total weight of the filtrate-filled container. The liquid phase may now be either analyzed (See Steps 8.13 and 8.14), or stored at 4°C until time of analysis. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample (See Step 8.4). Record the final weight of the liquid and solid phases.

8.11 The following details how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.6).

8.11.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the amount of fluid introduced into the device equals 20 times the weight of the solid phase of the waste that is in the ZHE.

8.11.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve, and disconnect the extraction fluid line. Check the ZHE to make sure that all valves are in their closed positions. Pick up the ZHE and physically rotate the device in an end-over-end fashion 2 or 3 times.

Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Put 5–10 psi behind the piston (if necessary), and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5–10 psi and check all ZHE fittings to insure that they are closed.

8.11.3 Place the ZHE in the rotary extractor apparatus (if it is not already there), and rotate the ZHE at 30 + 2 rpm for 18 hours. The temperature shall be maintained at 22 ± + 3°C during agitation.

8.12 Following the 18 hour extraction, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve, and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Replace ZHE O-rings or other fittings, as necessary, and redo the extraction with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR* bag, gas-tight syringe) holding the initial liquid phase of the waste, unless doing so would create multiple phases, or unless there is not enough volume left within the filtrate collection container. A separate filtrate collection container must be used in these cases. Filter through the glass fiber filter, using the ZHE device as discussed in Step 8.8. All extract shall be filtered and collected if the extract is multi-phasic or if the waste contained an initial liquid phase.

Note.—If the glass fiber filter is not intact following agitation, the filtration device discussed in the NOTE in Section 4.3.1 may be used to filter the material within the ZHE.

8.13 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 8.12 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Step 8.12, and the initial liquid phase (Step 8.8) are collectively defined as the TCLP extract.

8.14 The TCLP extract will be prepared and analyzed according to the appropriate SW–846 analytical methods, as identified in Appendix III of 40 CFR 261. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to 0.1 ml), conduct the appropriate analyses and combine the results mathematically by using a simple volume weighted average:

$$\text{Final contaminant concentration} = \frac{(V_1)(C_1)+(V_2)(C_2)}{V_1+V_2}$$

where:

V_1 = The volume of the first phase (l)
C_1 = The concentration of the contaminant of concern in the first phase (mg/l)
V_2 = The volume of the second phase (l)
C_2 = The concentration of the contaminant of concern in the second phase (mg/l)

8.15 The contaminant concentrations in the TCLP extract are compared to the thresholds identified in the appropriate regulations. Refer to Section 9 for quality assurance requirements.

9.0 *Quality Assurance requirements.*

9.1 All data, including quality assurance data, should be maintained and available for reference or inspection.

9.2 A minimum of one blank for every 10 extractions that have been conducted in an extraction vessel shall be employed as a check to determine if any memory effects from the extraction equipment is occurring. One blank shall also be employed for every new batch of leaching fluid that is made up.

9.3 All quality control measures described in the appropriate analytical methods shall be followed.

9.4 The method of standard addition shall be employed for each waste type if: 1) Recovery of the compound from spiked splits of the TCLP extract is not between 50 and 150%, or 2) If the concentration of the constituent measured in the extract is within 20% of the appropriate regulatory threshold. If more than 1 extraction is being run on samples of the same waste, the method of standard addition need only be applied once and the percent recoveries applied to the remainder of the extractions.

9.5 TCLP extracts shall be analyzed within the following periods after generation: Volatiles—14 days, Semi-volatiles—40 days, Mercury—28 days, and other Metals—180 days.

TABLE 1.—VOLATILE CONTAMINANTS [1]

Compound	CASNO
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
n-Butyl alcohol	71-36-6
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] Includes compounds identified in both the Land Disposal Restrictions Rule and the Toxicity Characteristic.

TABLE 2.—SUITABLE ROTARY AGITATION APPARATUS [1]

Company	Location	Model
Associated Design and Manufacturing Co.	Alexandria, Virginia, (703) 549-5999.	4-vessel device. 6-vessel device.
Lars Lande Manufacturing.	Whitmore Lake, Michigan, (313) 449-4116.	10-vessel device.
IRA Machine Shop and Laboratory.	Santurce, Puerto Rico, (809) 752-4004.	16-vessel device.
EPRI Extractor		6-vessel device.[2]

[1] Any device which rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

[2] Although this device is suitable, it is not commercially made. It may also require retrofitting to accommodate ZHE devices.

TABLE 3.—SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS

Company	Location	Model No.
Associated Design and Manufacturing Co.	Alexandria, Virginia, (703) 549-5999.	3740-ZHB
Millipore Corp	Bedford, Massachusetts, (800) 225-3384	SD1P581C5

TABLE 4.—SUITABLE FILTER HOLDERS [1]

Company	Location	Model	Size (mm)
Nucleopore Corp	Pleasanton, California, (800) 982-7711.	425910 410400	142 47
Micro Filtration Systems.	Dublin, California, (415) 828-6010	302400	142
Millipore Corp	Bedford, Massachusetts, (800) 225-3384	YT30142HW XX1004700	142 47

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic contaminants are of concern.

TABLE 5.—SUITABLE FILTER MEDIA

Company	Location	Model	Pore size [1]
Whatman Laboratory Products, Inc.	Clifton, New Jersey (201) 773-5800.	GFF	0.7

[1] Nominal pore size.

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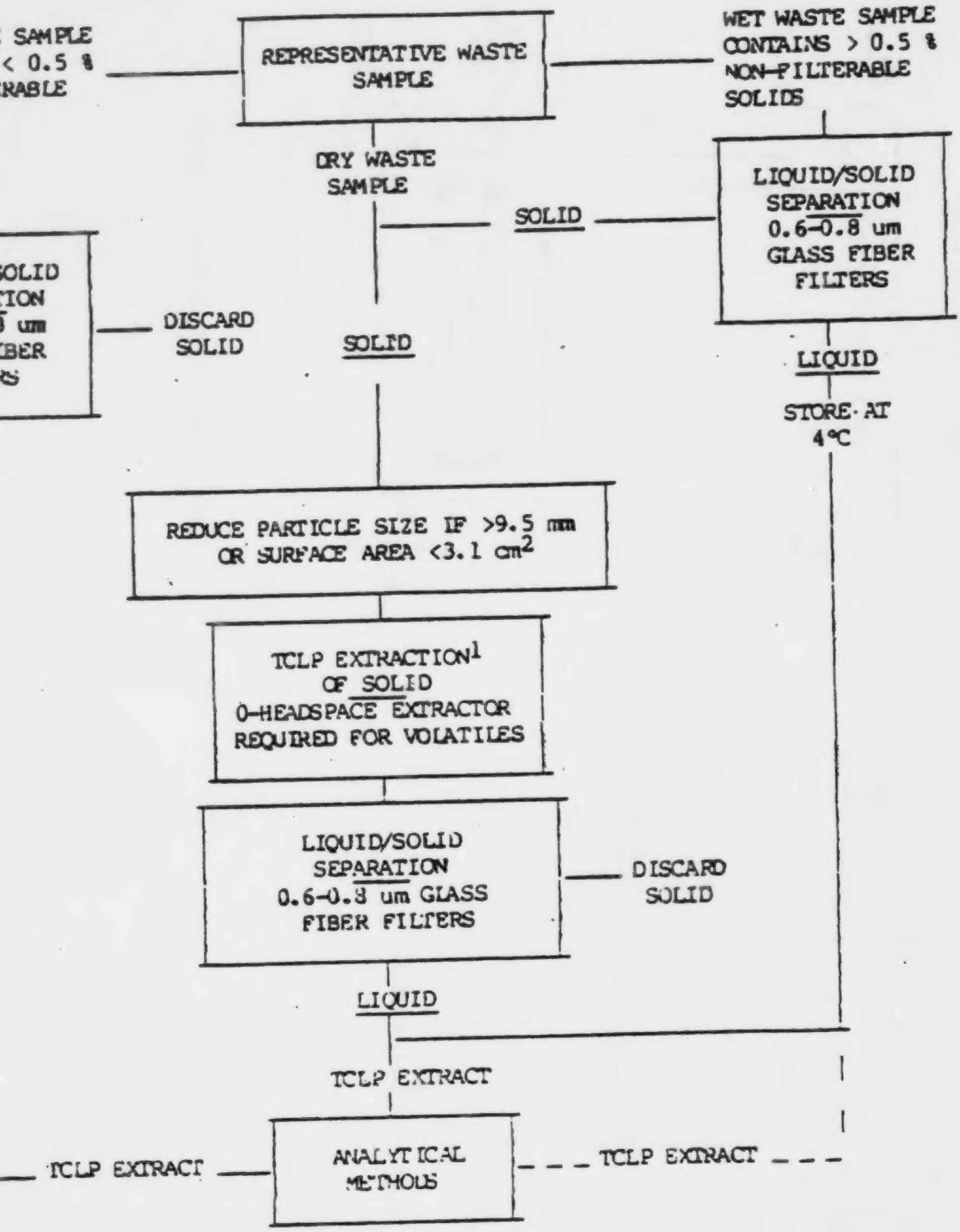
FIGURE 1: TCLP Flowchart


SAMPLE
< 0.5 %
ERABLE
REPRESENTATIVE WASTE SAMPLE
WET WASTE SAMPLE CONTAINS > 0.5 % NON-FILTERABLE SOLIDS
DRY WASTE SAMPLE
SOLID
LIQUID/SOLID SEPARATION 0.6-0.8 um GLASS FIBER FILTERS
SOLID
TION
3 um
IBER
RS
DISCARD SOLID
SOLID
LIQUID
STORE AT 4°C
REDUCE PARTICLE SIZE IF >9.5 mm OR SURFACE AREA <3.1 cm2
TCLP EXTRACTION1 OF SOLID 0-HEADSPACE EXTRACTOR REQUIRED FOR VOLATILES
LIQUID/SOLID SEPARATION 0.6-0.8 um GLASS FIBER FILTERS
DISCARD SOLID
LIQUID
TCLP EXTRACT
ANALYTICAL METHODS
TCLP EXTRACT
TCLP EXTRACT

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xtraction fluid employed is a function of the alkalinity of the solid
of the waste.

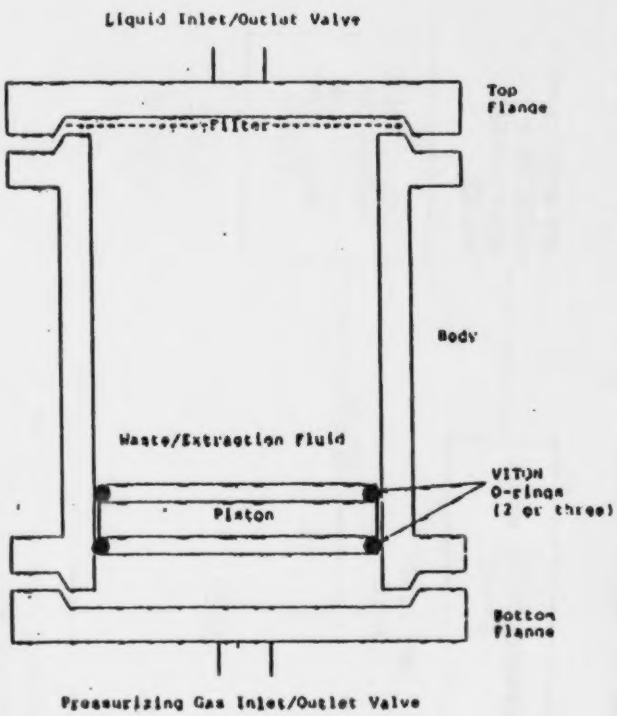
Liquid Inlet/Outlet Valve
Top Flange
Filter
Body
Waste/Extraction Fluid
VITON O-rings (2 or three)
Piston
Bottom Flange
Pressurizing Gas Inlet/Outlet Valve

Figure 3: Zero-Headspace Extraction Vessel

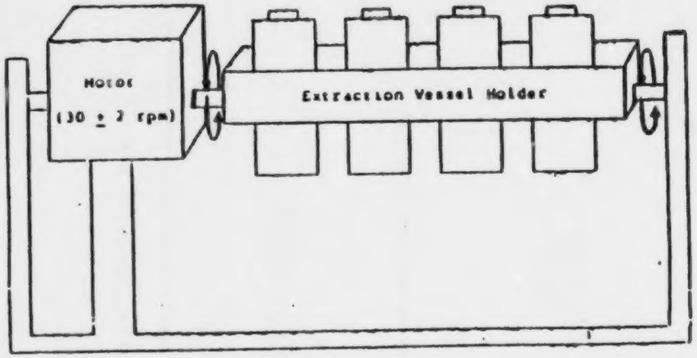
Motor (30 ± 2 rpm)
Extraction Vessel Holder

Figure 2: Rotary Agitation

BILLING CODE 6560-50-C

4. Amend Table 1 of Appendix III of Part 261 to add the following compounds and methods in alphabetical order:

Appendix III—Chemical Analysis Test Methods

* * * * *

TABLE 1.—ANALYSIS METHODS FOR ORGANIC CHEMICALS CONTAINED IN SW–846

Compound	First edition method(s)	Second edition method(s)
* * *	*	*
Benzene	8.02, 8.24	8020, 8024, 5030/8240
* * *	*	*
Bis(2-chloroethyl)ether	8.01, 8.24	8010, 8240, 3510/8270
* * *	*	*
Cresol(s)	8.04, 8.25	8040, 8250, 3510/8270
* * *	*	*
Dichlorobenzene(s)	8.01, 8.02, 8.12, 8.25	8010, 8120, 8250, 3519/8270
1,2-Dichloroethane	8.01, 8.24	8010, 8240, 5030/8240
1,1-Dichloroethylene		5030/8240
* * *	*	*
2,4-Dinitrotoluene	8.09, 8.25	8090, 8250, 3510/8270
* * *	*	*
Hexachlorobenzene	8.12, 8.25	8120, 8250, 3510/8270
Hexachlorobutadiene	8.12, 8.25	8120, 8250, 3510/8270
Hexachloroethane	8.12, 8.25	8010, 8240, 3510/8270
* * *	*	*
Isobutanol		5030/8240
* * *	*	*
Methoxychlor		8080
Methylene chloride		5030/8240
* * *	*	*
Nitrobenzene	8.09, 8.25	8090, 8250, 3510/8270

TABLE 1.—ANALYSIS METHODS FOR ORGANIC CHEMICALS CONTAINED IN SW–846—Continued

Compound	First edition method(s)	Second edition method(s)
* * *	*	*
Pentachlorophenol	8.04, 8.25	8040, 8250, 3510/8270
Phenol	8.04, 8.25, 8.22	8040, 8250, 8140, 3510/8270
* * *	*	*
Pyridine	8.06, 8.09, 8.25	8090, 8250, 3510/8270
* * *	*	*
Tetrachloroethane(s)	8.01, 8.24	8010, 8240, 5030/8240
* * *	*	*
Tetrachloroethylene		5030/8240
Tetrachlorophenol(s)	8.04, 8.24	8040, 8250, 3510/8270
Toluene	8.02, 8.24	8020, 8024, 5030/8240
* * *	*	*
Trichloroethane(s)	8.01, 8.24	8010, 8240, 5030/8240
Trichloroethylene		5030/8240
* * *	*	*
Trichlorophenol(s)	8.04, 8.25	8040, 8250, 3510/8270
* * *	*	*

PART 271—REQUIREMENTS FOR AUTHORIZATION OF STATE HAZARDOUS WASTE PROGRAMS

1. The authority citation for Part 271 continues to read as follows:

Authority: Secs. 1006, 2002(a), and 3006 of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976, as amended (42 U.S.C. 6905, 6912(a), and 6926).

2. Amend § 271.1 Paragraph (j) by adding the following entry to Table 1 in chronological order by date of publication:

§ 271.1 Purpose and scope.

* * * * *

(j) * * *

TABLE 1.—REGULATIONS IMPLEMENTING THE HAZARDOUS AND SOLID WASTE AMENDMENTS OF 1984

Date	Title of regulation
* * *	* *
June 13, 1986	Toxicity Characteristic.
* * *	* *

PART 302—DESIGNATION, REPORTABLE QUANTITIES, AND NOTIFICATION

1. The authority citation for Part 302 continues to read as follows:

Authority: Sec. 102 of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, 42 U.S.C. 9602; Secs. 311 and 501(a) of the Federal Water Pollution Control Act, 33 U.S.C. 1321 and 1361.

2. Section 302.4 is amended by revising the entry for "Characteristic of EP Toxicity" in Table 302.4 and the footnotes are republished as follow:

§ 302.4 Designation of hazardous substances.

* * * * *

TABLE 302.4.—LIST OF HAZARDOUS SUBSTANCES AND REPORTABLE QUANTITIES

Hazardous substance	CASRN	Regulatory synonyms	Statutory			Final RQ	
			RQ	Code†	RCRA waste No.	Category	Pounds (Kg)
*	*	* *	*				
Unlisted Hazardous Wastes			1*	4			
*	*	* *	*				
Toxicity Characteristic			1*	4			
Acrylonitrile	107131	2-Propenenitrile	100	1,2,4	D018	B	100#(45.4)
Arsenic			1*	4	D004	X	1#(0.454)
Barium			1*	4	D005	C	1000(454)
Benzene	71432		1000	1,2,3,4	D019	C	1000#(454)
Bis(2-chloroethyl) ether	111444	Dichloroethyl ether Ethane, 1,1'-oxybis[2-chloro-	1*	2,4	D020	X	1#(0.454)
Cadmium			1*	4	D006	X	1#(0.454)
Carbon disulfide	75150	Carbon bisulfide	5000	1,4	D021	D	5000##(2270)
Carbon tetrachloride	56235	Methane, tetrachloro-	5000	1,2,4	D022	D	5000#(2270)
Chlordane	57749	Chlordane, technical 4,7-Methanoindan, 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-	1	1,2,4	D023	X	1#(0.454)
Chlorobenzene	108907	Benzene, chloro-	100	1,2,4	D024	B	100(45.4)
Chloroform	67663	Methane, trichloro-	5000	1,2,4	D025	D	5000#(2270)
Chromium			1*	4	D007	X	1#(0.454)
o-Cresol	95487	o-Cresylic acid	1000	1,4	D026	C	1000##(454)
m-Cresol	108394	m-Cresylic acid	1000	1,4	D027	C	1000##(454)
p-Cresol	106445	p-Cresylic acid	1000	1,4	D028	C	1000##(454)
2,4-D			100	1,4	D016	B	100(45.4)
1,2-Dichlorobenzene	95501	Benzene, 1,2-dichloro-o-Dichlorobenzene	100	1,2,4	D029	B	100(45.4)
1,4-Dichlorobenzene	106467	Benzene, 1,4-dichloro-p-Dichlorobenzene	100	1,2,4	D030	B	100(45.4)
1,2-Dichloroethane	107062	Ethane, 1,2-dichloro-Ethylene dichloride	5000	1,2,4	D031	D	5000#(2270)
1,1-Dichloroethylene	75354	Ethene, 1,1-dichloro-Vinylidene chloride	5000	1,2,4	D032	D	5000#(2270)
2,4-Dinitrotoluene	121142	Benzene, 1-methyl-2,4-dinitro-	1000	1,2,4	D033	C	1000#(454)
Endrin			1	1,4	D012	X	1(0.454)
Heptachlor (and hydroxide)	76448	4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	1	1,2,4	D034	X	1#(0.454)
Hexachlorobenzene	118741	Benzene, hexachloro-	1*	2,4	D035	X	1#(0.454)
Hexachlorobutadiene	87683	1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	1*	2,4	D036	X	1#(0.454)
Hexachloroethane	67721	Ethane, 1,1,1,2,2,2-hexachloro-	1*	2,4	D037	X	1#(0.454)
Isobutanol	78831	Isobutyl alcohol 1-Propanol, 2-methyl-	1*	4	D038	D	5000(2270)
Lead			1*	4	D008	X	1##(0.454)

TABLE 302.4.—LIST OF HAZARDOUS SUBSTANCES AND REPORTABLE QUANTITIES—Continued

Hazardous substance	CASRN	Regulatory synonyms	Statutory			Final RQ	
			RQ	Code†	RCRA waste No.	Category	Pounds (Kg)
Lindane			1	1,4	D013	X	1#(0.454)
Mercury			1*	4	D009	X	1(0.454)
Methoxychlor			1	1,4	D014	X	1(0.454)
Methylene chloride	75092	Methane, dichloro-	1*	2,4	D039	C	1000(454)
Methyl ethyl ketone	78933	2-Butanone	1*	4	D040	D	5000(2270)
Nitrobenzene	98953	Benzene, nitro-	1000	1,2,4	D041	C	1000(454)
Pentachlorophenol	87865	Phenol, pentachloro-	10	1,2,4	D042	A	10#(4.54)
Phenol	108952	Benzene, hydroxy-	1000	1,2,4	D043	C	1000##(454)
Pyridine	110861		1*	4	D044	X	1##(0.454)
Selenium			1*	4	D010	X	1##(0.454)
Silver			1*	4	D011	X	1(0.454)
1,1,1,2-Tetrachloroethane	630206	Ethane, 1,1,1,2-tetrachloro-	1*	4	D045	X	1#(0.454)
1,1,2,2-Tetrachloroethane	79345	Ethane, 1,1,2,2-tetrachloro-	1*	2,4	D046	X	1#(0.454)
Tetrachloroethylene	127184	Ethene, 1,1,2,2-tetrachloro-	1*	2,4	D047	X	1#(0.454)
2,3,4,6-Tetrachlorophenol	58902	Phenol, 2,3,4,6-tetrachloro-	1*	4	D048	A	10(4.54)
Toluene	108883	Benzene, methyl-	1000	1,2,4	D049	C	1000(454)
Toxaphene			1	1,4	D015	X	1#(0.454)
1,1,1-Trichloroethane	71556	Methyl chloroform	1*	2,4	D050	C	1000(454)
1,1,2-Trichloroethane	79005	Ethane, 1,1,2-trichloro-	1*	2,4	D051	X	1#(0.454)
Trichloroethylene	79016	Trichloroethene	1000	1,2,4	D052	C	1000#(454)
2,4,5-Trichloro-phenol	95954	Phenol, 2,4,5-trichloro-	10	1,4	D053	A	10#(4.54)
2,4,6-Trichloro-phenol	88062	Phenol, 2,4,6-trichloro-	10	1,2,4	D054	A	10#(4.54)
2,4,5-TP			100	1,4	D017	B	100(45.4)
Vinyl chloride	75014	Ethene, chloro-	1*	2,3,4	D055	X	1#(0.454)

†—Indicates the statutory source as defined by 1,2,3, or 4 below.
1—Indicates that the statutory source for designation of the hazardous substance under CERCLA is CWA Section 311(b)(4).
2—Indicates that the statutory source for designation of the hazardous substance under CERCLA is CWA Section 307(a).
3—Indicates that the statutory source for designation of the hazardous substance under CERCLA is CAA Section 112.
4—Indicates that the statutory source for designation of the hazardous substance under CERCLA is RCRA Section 3001.

1*—Indicates that the 1-pound RQ is a CERCLA statutory RQ.

#—Indicates that the RQ is subject to change when the assessment of potential carcinogenicity and/or chronic toxicity is completed.
##—Indicates that an adjusted RQ is proposed in a separate NPRM (50 FR 13154, April 4, 1985).
###—The Agency may adjust the RQ for methyl isocyanate in a future rulemaking; until then the statutory 1-pound RQ applies.

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BILLING CODE 6560-50-M

EPA METHOD
NO. 245.5

MERCURY IN SEDIMENT

Method 245.5 (Manual Cold Vapor Technique)

1. Scope and Application
   - 1.1 This procedure(1) measures total mercury (organic + inorganic) in soils, sediments, bottom deposits and sludge type materials.
   - 1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.
2. Summary of Method
   - 2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
   - 2.2 An alternate digestion(2) involving the use of an autoclave is described in (8.2).
3. Sample Handling and Preservation
   - 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
   - 3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.
4. Interferences
   - 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
   - 4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the BOD bottle should be purged before the addition of stannous sulfate.
5. Apparatus
   - 5.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

     NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

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5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4–1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.

NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 ug/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution (6.7) containing 0 to 1.0 ug of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of $KMnO_4$ solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass value and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass value, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave., and North Cassidy St., Columbus, Ohio 43219. Cat. #580-13 or #580-22.

8. Procedure

8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a BOD bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated $KMnO_4$ solution is added and the bottle covered with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

9. Calculation
   9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.
   9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\,Hg/g = \frac{ug\,Hg \text{ in the aliquot}}{\text{wt of the aliquot in gms}}$$

   9.3 Report mercury concentrations as follows: Below 0.1 *ug*/gm, <0.1; between 0.1 and 1 *ug*/gm, to the nearest 0.01 *ug*; between 1 and 10 *ug*/gm, to nearest 0.1 *ug*; above 10 *ug*/gm, to nearest *ug*.

10. Precision and Accuracy
    10.1 The following standard deviations on replicate sediment samples were recorded at the indicated levels; 0.29 *ug*/g ±0.02 and 0.82 *ug*/g ±0.03. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97% and 94%, respectively.

Bibliography

1. Bishop, J. N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.
2. Salma, M., private communication, EPA Cal/Nev Basin Office, Almeda, California.

EPA METHOD
NO. 3020

METHOD 3020

ACID DIGESTION PROCEDURE FOR FURNACE ATOMIC ABSORPTION SPECTROSCOPY

1.0 Scope and Application

1.1 This digestion procedure is approved for the preparation of aqueous samples, mobility procedure extracts, and certain nonaqueous wastes for analysis, by furnace atomic absorption spectroscopy (AAS), for the metals listed below. The procedure is to be used when one is to determine the total amount of the metal in the sample.

1.2 Metals for which Method 3020 is the approved furnace AAS procedure are:

Aluminum
Barium
Beryllium
Cadmium
Chromium
Cobalt
Copper
Iron
Lead
Manganese
Molybdenum
Nickel
Silver
Thallium
Vanadium
Zinc

1.3 If a nonaqueous sample is not completely digested by this method and determination as to the total concentration of a metal in the entire sample is required, then the digestion methods described in Method 3030, 3040, or 3050 should be tried. Some wastes will require fusion techniques to completely release metals from inorganic matrices. The appropriate fusion method should be chosen from the literature and its applicability to the sample of interest proven by analyzing spiked samples and relevant standard reference materials.

2.0 Summary of Method

2.1 A mixture of nitric acid and the material to be analyzed is heated to near dryness in a Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to near dryness, it is cooled and brought up in dilute nitric acid such that the final dilution contains 0.5% (v/v) HNO_3.

3.0 Interferences

3.1 Interferences are discussed in the referring analytical method.

4.0 Apparatus and Materials

4.1 Griffin beakers of assorted sizes.

4.2 Qualitative filter paper or centrifugation equipment.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Aqueous wastewaters must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc. HNO_3. Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc. HNO_3. Re-cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. It should be noted that if a sample is allowed to go to dryness, low recoveries may result for tin and antimony.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3, and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with distilled water and when necessary filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute nitric acid. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

EPA METHOD
NO. 204.2

ANTIMONY

Method 204.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

num Concentration Range: 20–300 ug/l
ction Limit: 3 ug/l

aration of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.2% (v/v) HNO_3.

le Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

le Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual should be followed including the addition of sufficient 1:1 HCl to dissolve the digested residue for the analysis of suspended or total antimony. The sample solutions used for analysis should contain 2% (v/v) HNO_3.

ument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–800°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

sis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

EPA METHOD
NO. 206.2

ARSENIC

Method 206.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

Optimum Concentration Range: 5–100 ug/l
Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/1).

2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100ml.

3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2ml of 30% H_2O_2 and 2ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.

2. Cool and bring back to 50 ml with deionized distilled water.

3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace.

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NOTE: If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30%H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1100°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *u*g/l.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent containing 15 *u*g/l and spiked with concentrations of 2, 10 and 25 *u*g/l, recoveries of 85%, 90% and 88% were obtained respectively. The relative standard deviation at these concentrations levels were ±8.8%, ±8.2%, ±5.4% and ±8.7%, respectively.
2. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 20, 50 and 100 *u*g As/l, the standard deviations were ±0.7, ±1.1 and ±1.6 respectively. Recoveries at these levels were 105%, 106% and 101%, respectively.

EPA METHOD
NO. 270.2

SELENIUM

Method 270.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

Optimum Concentration Range: 5–100 ug/l
Detection Limit: 2 ug/l

Preparation of Standard Solution

1. Stock Selenium Solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/1).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Selenium Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace. NOTE: If solubilization or digestion is not required adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

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Instrument Parameters

1. Drying time and temperature: 30 sec @ 125°C
2. Charring time and temperature: 30 sec @ 1200°C
3. Atomizing time and temperature: 10 sec @ 2700°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Selenium analysis suffers interference from chlorides (> 800 mg/1) and sulfate (> 200 mg/1). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/1, both samples and standards should be prepared to contain 1% nickel.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Using a sewage treatment plant effluent containing < 2 *ug*/1 and spiked with a concentration of 20 *ug*/1, a recovery of 99% was obtained.
2. Using a series of industrial waste effluents spiked at a 50 *ug*/1 level, recoveries ranged from 94 to 112%.
3. Using a 0.1% nickel nitrate solution as a synthetic matrix with selenium concentrations of 5, 10, 20, 40, 50, and 100 *ug*/1, relative standard deviations of 14.2, 11.6, 9.3, 7.2, 6.4 and 4.1%, respectively, were obtained at the 95% confidence level.

4. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 20 ug Se/1, the standard deviations were ±0.6, ±0.4, and ±0.5, respectively. Recoveries at these levels were 92%, 98%, and 100%, respectively.

Reference:

"Determining Selenium in Water, Wastewater, Sediment and Sludge By Flameless Atomic Absorption Spectroscopy", Martin, T. D., Kopp, J. F. and Ediger, R. D. Atomic Absorption Newsletter 14, 109 (1975).

EPA METHOD
NO. 272.2

SILVER

Method 272.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01077
Dissolved 01075
Suspended 01076

Optimum Concentration Range: 1–25 ug/l
Detection Limit: 0.2 ug/l

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec -2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Background correction may be required if the sample contains high dissolved solids.
3. The use of halide acids should be avoided.
4. If adsorption to container walls or formation of AgCl is suspected, see NOTE 3 under the Direct Aspiration Method 272.1.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
8. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy:

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 25, 50, and 75 ug Ag/1, the standard deviations were ±0.4, ±0.7, and ±0.9, respectively. Recoveries at these levels were 94%, 100% and 104%, respectively.

EPA METHOD
NO. 279.2

THALLIUM

Method 279.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01059
Dissolved 01057
Suspended 01058

Optimum Concentration Range: 5–100 ug/l
Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C
3. Atomizing Time and Temp: 10 sec @ 2400°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ACID DIGESTION
(FROM CLP SOW NO. 785)

ATTACHMENT 1

SAMPLE PREPARATION OF SEDIMENTS, SLUDGES AND SOILS

1. Scope and Application

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

Aluminum
Antimony
Arsenic
Barium
Beryllium
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Nickel
Potassium
Selenium
Silver
Sodium
Thallium
Vanadium
Zinc

2. Summary of Method

NOTE: A separate digestion procedure is required for furnace AA and ICP analysis.

2.1 A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a total solids determination (Exhibit D, Attachment 9).

3. Apparatus and Materials

3.1 250 ml beaker or other appropriate vessel.

3.2 Watch glasses

3.3 Thermometer that covers range of 0° to 200°C

3.4 Whatman No. 42 filter paper or equivalent

4. Reagents

4.1 ASTM Type II water (ASTM D1193): Water must be monitored.

4.2 Concentrated Nitric Acid (sp. gr. 1.41)

4.3 Concentrated Hydrochloric Acid (sp. gr. 1.19)

4.4 Hydrogen Peroxide (30%)

5. Sample Preservation, and Handling

5.1 Non-aqueous samples must be refrigerated upon receipt until analysis.

6. Procedure

6.1 Mix the sample thoroughly to achieve homogeniety. For each digestion procedure, weigh (to the nearest 0.01gms) a 1.0 to 1.5 gm portion of sample and transfer to a beaker.

6.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

6.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

6.4 Continue to add 30% H_2O_2 in 1 ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml 30% H_2O_2.)

6.5 If the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample - see Note 1). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Dilute the digestate 1:1 (200 ml final volume) with the deionized water. The sample is now ready for analysis.

6.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture After cooling, filter through Whatman No. 42 filter paper (or equivalent - see Note 1) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3. Dilute the digestate 1:1 (200 mL final volume) with deionized water. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

7. Calculations

7.1 A separate determination of percent solids must be performed (Exhibit D, Attachment 9).

7.2 The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

where C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample
S = % Solids/100

REF: Modification of Method 3050 from SW-846, Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

8. Bibliography

1. Modification (by committee) of Method 3050, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

EPA METHOD
NO. 200.7M

~~$MDL = 2.681 (S_{pooled})$~~

~~where 2.681 is equal to $t_{(12,\ 1-\alpha\ =\ .99)}$.~~

~~(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.~~

~~$LCL = 0.72\ MDL$~~

~~$UCL = 1.65\ MDL$~~

~~where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.~~

~~TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL~~

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
∞	∞	2.326

~~Reporting~~

~~The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.~~

~~If the level of analyte in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.~~

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.12 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 7.5.1)

3.14 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1.)

4. Safety

4.1 The toxicity of carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is reponsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [14.7, 14.8 and 14.9] for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena, and (4) background.contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interferenece from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The Interference information, which was collected at the Ames Laboratory,[1] is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2–5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 *Physical interferences* are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aersol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 *Chemical Interferences* are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

5.2.1 *Serial dilution*—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit (14.3) that has been established for that matrix.). If not, a chemical or physical interference effect should be suspected.

5.2.2 *Spike addition*— The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Caution: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (See 5.2.3).

5.2.3 *Comparison with alternate method of analysis*—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

5.2.4 *Wavelength scanning of analyte line region*—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

6.1.1 Computer controlled atomic emission spectrometer with background correction.

6.1.2 Radiofrequency generator.

6.1.3 Argon gas supply, welding grade or better.

6.2 Operating conditions—Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and Standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 *Acetic acid*, conc. (sp gr 1.06).

7.1.2 *Hydrochloric acid*, conc. (sp gr 1.19).

7.1.3 *Hydrochloric acid*, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

7.1.4 *Nitric acid*, conc. (sp gr 1.41).

7.1.5 *Nitric acid*, (1+1): Add 500 mL conc. HNO_3 (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 *Deionized, distilled water:* Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105 °C unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.)

Typical stock solution preparation procedures follow:

7.3.1 *Aluminum solution, stock*, 1 mL = µg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask add an additional 10 mL of (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.2 *Antimony solution stock*, 1 mL = 100 µg Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.3 *Arsenic solution, stock*, 1 mL = 100 µg As: Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

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[1] Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011

7.3.4 *Barium solution, stock,* 1 mL = 100 µg Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250 °C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 with mL deionized, distilled water.

7.3.5 *Beryllium solution, stock,* 1 mL = 100 µg Be: *Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.6 *Boron solution, stock,* 1 mL = 100 µg B: *Do not dry.* Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 *Cadmium solution, stock,* 1 mL = 100 µg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.8 *Calcium solution, stock,* 1 mL = 100 µg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180 °C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.9 *Chromium solution, stock,* 1 mL = 100 µg Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.10 *Cobalt solution, stock,* 1 mL = 100 µg Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.11 *Copper solution, stock,* 1 mL = 100 µg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.12 *Iron solution, stock,* 1 mL = 100 µg Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.13 *Lead solution, stock,* 1 mL = 100 µg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.14 *Magnesium solution, stock,* 1 mL = 100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.15 *Manganese solution, stock,* 1 mL = 100 µg Mn: Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

7.3.16 *Molybdenum solution, stock,* 1 mL = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

7.3.17 *Nickel solution, stock,* 1 mL = 100 µg Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1,000 mL with deionized, distilled water.

7.3.18 *Potassium solution, stock,* 1 mL = 100 µg K: Dissolve 0.1907 g KCl, dried at 110 °C, in deionized, distilled water and dilute to 1,000 mL.

7.3.19 *Selenium solution, stock,* 1 mL = 100 µg Se: *Do not dry.* Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

7.3.20 *Silica solution, stock,* 1 mL = 100 µg SiO_2: *Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.21 *Silver solution, stock,* 1 mL = 100 µg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1,000 mL with deionized, distilled water.

7.3.22 *Sodium solution, stock,* 1 mL = 100 µg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.23 *Thallium solution, stock,* 1 mL = 100 µg Tl: Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.24 *Vanadium solution, stock,* 1 mL = 100 µg V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.25 *Zinc solution, stock,* 1 mL = 100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL deionized, distilled water.

7:4 *Mixed calibration standard solutions*—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HC1 and dilute to 100 mL with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

7.4.1 *Mixed standard solution I*—Manganese, beryllium, cadmium, lead, and zinc.

7.4.2 *Mixed standard solution II*—Barium, copper, iron, vanadium, and cobalt.

7.4.3 *Mixed standard solution III*—Molybdenum, silica, arsenic, and selenium.

7.4.4 *Mixed standard solution IV*—Calcium, sodium, potassium, aluminum, chromium and nickel.

7.4.5 *Mixed standard solution V*—Antimony, boron, magnesium, silver, and thallium.

Note 1.—If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 *The calibration blank* is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 *The reagent blank* must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8) and a quality control sample (3.9) are also required for the analyses.

7.6.1 The *instrument check standard* is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 12.1.1.)

7.6.2 The *interference check sample* is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest but known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/L or 5 times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 12.1.2).

7.6.3 The *quality control sample* should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 12.1.3.)

8. Sample Handling and Preservation

8.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See Notes 2 and 3).

Note 2.—Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

Note 3.—If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50–100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

8.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 9.3.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc. HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, and 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See Note 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

Note 4.—In place of filtring, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 mL of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gently reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total."

Note 5.—If low determinations of boron are critical, quartz glassware should be used.

Note 6.—If the sample analysis solution has a different acid concentration from that given in 9.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

10. Procedure

10.1 Set up instrument with proper operating parameters established in Section 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

Note 7.—For boron concentrations greater than 500 μg/L extended flush times of 1 to 2 minutes may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See Note 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 samples.

10.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (14.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus

fferent slope from that of the
ndards. It will not correct for
erence which causes a baseline
lest version of this technique is
tion method. The procedure is
o identical aliquots of the
n. each of volume V_x, are
irst (labeled A) is added a
$/_s$ of a standard analyte
centration c_s. To the second
dded the same volume V_s of
e analytical signals of A and B
and corrected for nonanalyte
known sample concentration
d:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B)\ V_x}$$

S_B are the analytical signals
he blank) of solutions A and B.
, and c_s should be chosen so
ly twice S_B on the average. It
nade much less than V_x, and
greater than c_x, to avoid
of the sample matrix. If a
oncentration step is used, the
est made first and carried
ire procedure. For the results
ique to be valid, the following
t be taken into consideration:
ical curve must be linear.
cal form of the analyte added
he same as the analyte in the

rence effect must be constant
g range of concern.
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rence.

t blanks (7.5.2) should be
all samples. This is
ortant for digested samples
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or must be applied to sample

ould be rounded to the
e and all results should be
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trol (Instrumental)

he instrument standardization
propriate quality control
as follow:

12.1.1 Analyze and appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ±5% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within the established control limits of 2 standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors analyze the interference check sample (7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.3 A quality control sample (7.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within ±5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

13. Precision and Accuracy

13.1 In an EPA round robin phase 1 study, even laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

14. References

14.1 Winge, R.K., V.J. Peterson, and V.A. Fassel, "Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines," EPA–600/4–79–017.

14.2 Winefordner, J.D., "Trace Analysis: Spectroscopic Methods for Elements," *Chemical Analysis*, Vol. *46*, pp. 41–42.

14.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA–600/4–79–019.

14.4 Garbarino, J.R. and Taylor, H.E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," Applied Spectroscopy *33*, No. 3 (1979).

14.5 "Methods for Chemical Analysis of Water and Wastes," EPA–600/4–79–020.

14.6 Annual Book of ASTM Standards, Part 31.

14.7 "Carcinogens—Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77–206, Aug. 1977

14.8 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

14.9 "Safety in Academic Chemistry Laboratories, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

TABLE 1.—RECOMMENDED WAVELENGTHS [1] and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, µg/L [2]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	[3]
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[1] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1).

[2] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA–600/4–79–017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[3] Highly dependent on operating conditions and plasma position.

TABLE 1.—ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

Analyte	Wavelength, nm	Interferent—									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
	308.214							0.21			1.4
	206.833	0.47		2.9		0.08				0.25	0.45
	193.696	1.3		0.44							1.1
	455.403										
	313.042									0.04	0.05
	249.773	0.04				0.32					
	226.502					0.03			0.02		
	317.933			0.08		0.01	0.01	0.04		0.03	0.03
	267.716					0.003		0.04			0.04
	228.616			0.03		0.005			0.03	0.15	
	324.754					0.003				0.05	0.02
	259.940							0.12			

TABLE 1.—ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL—Continued

Analyte	Wavelength, nm	Interferent— Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Lead	220.353	0.17									
Magnesium	279.079		0.02	0.11		0.13		0.25		0.07	0.12
Manganese	257.610	0.005		0.01		0.002	0.002				
Molybdenum	202.030	0.05				0.03					
Nickel	231.604										
Selenium	196.026	0.23				0.09					
Silicon	288.158			0.07							0.01
Sodium	588.995									0.08	
Thallium	190.864	0.30									
Vanadium	292.402			0.05		0.005				0.02	
Zinc	213.856				0.14				0.29		

TABLE 3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1,000
AS	10	Ca	1,000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1,000
Ca	1	Mg	1,000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Tl	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

TABLE 4.—ICP PRECISION AND ACCURACY DATA

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True value μg/L	Mean reported value μg/L	Mean percent RSD	True value μg/L	Mean reported value μg/L	Mean percent RSD	True value μg/L	Mean reported value μg/L	Mean percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

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SUPERSCAN ELEMENTS, WAVELENGTHS, & LTL

Element	Symbol	Wavelength*	LTL (mg/l)**
Aluminum	Al-SS	396.152	0.1
Antimony	Sb-SS	206.833	1
Arsenic	As-SS	197.197	1
Barium	Ba-SS	455.403	0.1
Beryllium	Be-SS	313.042	0.1
Bismuth	Bi-SS	223.061	0.5
Boron	B-SS	249.773	0.1
Cadmium	Cd-SS	214.438	0.1
Calcium	Ca-SS	393.366	0.1
Cerium	Ce-SS	413.765	1
Chromium	Cr-SS	205.552	0.1
Cobalt	Co-SS	238.892	0.1
Copper	Cu-SS	324.754	0.1
Dysprosium	Dy-SS	353.170	0.1
Erbium	Er-SS	349.910	0.1
Europium	Eu-SS	381.967	0.1
Gadolinium	Gd-SS	342.247	0.5
Gallium	Ga-SS	294.364	0.5
Germanium	Ge-SS	265.118	0.5
Gold	Au-SS	242.765	1
Hafnium	Hf-SS	277.336	1
Holmium	Ho-SS	345.600	0.5
Indium	In-SS	230.606	1
Iodine	I-SS	183.038	1
Iridium	Ir-SS	224.268	1
Iron	Fe-SS	238.204	0.1
Lanthanum	La-SS	379.478	0.1
Lead	Pb-SS	220.353	0.5
Lithium	Li-SS	670.781	0.1
Lutetium	Lu-SS	261.542	0.1
Magnesium	Mg-SS	279.553	0.1
Manganese	Mn-SS	257.610	0.1
Mercury	Hg-SS	194.232	0.5
Molybdenum	Mo-SS	202.030	0.5
Neodymium	Nd-SS	309.418	0.5
Nickel	Ni-SS	231.604	0.1
Niobium	Nb-SS	401.225	1
Osmium	Os-SS	228.226	0.1
Palladium	Pd-SS	340.458	0.5
Phosphorus	P-SS	213.618	1
Platinum	Pt-SS	214.423	1
Potassium	K-SS	766.490	1
Praseodymium	Pr-SS	390.844	1
Rhenium	Re-SS	221.426	1
Rhodium	Rh-SS	233.477	1
Ruthenium	Ru-SS	240.272	1
Samarium	Sm-SS	359.260	0.5
Scandium	Sc-SS	361.384	0.1
Selenium	Se-SS	196.079	1
Silicon	Si-SS	251.611	0.1
Silver	Ag-SS	328.068	0.1
Sodium	Na-SS	589.595	0.1
Strontium	Sr-SS	407.771	0.1
Sulfur	S-SS	180.731	1
Tantalum	Ta-SS	226.230	0.5
Tellurium	Te-SS	214.281	1
Terbium	Tb-SS	350.917	0.5
Thallium	Tl-SS	334.941	1
Thorium	Th-SS	283.730	1
Thulium	Tm-SS	313.126	0.5
Tin	Sn-SS	189.989	0.5
Titanium	Ti-SS	334.941	0.1
Tungsten	W-SS	207.911	1
Uranium	U-SS	385.958	1
Vanadium	V-SS	292.402	0.5
Ytterbium	Yb-SS	328.937	0.1
Yttrium	Y-SS	371.030	0.1
Zinc	Zn-SS	213.856	0.1
Zirconium	Zr-SS	343.823	0.1

* Wavelength: Most sensitive line for analysis. Line choice is dependent on sample matrix. Use of secondary lines is necessary for some elements for spectral interference confirmation.

** LTL: Lower Threshold Limit. Based upon Signal-to-Noise Ratio for each element; expressed as mg/l. Lower levels would be recorded as ND. The LTL for each analyte is highly dependent upon sample matrix and subject to change on a sample-by-sample basis.

EPA METHOD
NO. 350.2

NITROGEN, AMMONIA

Method 350.2 (Colorimetric; Titrimetric; Potentiometric – Distillation Procedure)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
   1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
   1.2 The method covers the range from about 0.05 to 1.0 mg NH_3–N/l for the colorimetric procedure, from 1.0 to 25 mg/l for the titrimetric procedure, and from 0.05 to 1400 mg/l for the electrode method.
   1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
   2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
   4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
   4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.
   4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

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5. Apparatus

5.1 An all-glass distilling apparatus with an 800–1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ± 1.5 mm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/1): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg NH_3–N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water.

NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1000 ml with CO_2-free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3–N	mg NH_3–N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH_3–N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3 - N = \frac{A \times 0.28 \times 1{,}000}{S}$$

where:

A = ml 0.02 N H_2SO_4 used.
S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l } NH_3 - N = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3–N read from standard curve.
B = ml total distillate collected, including boric acid and dilution.
C = ml distillate taken for nesslerization.
D = ml of original sample taken.

8.3 Potentiometric

$$\text{mg/l NH}_3 - \text{N} = \frac{500}{\text{D}} \times \text{A}$$

where:

A = mg NH_3–N/1 from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mgN/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.21	0.122	–5.54	–0.01
0.26	0.070	–18.12	–0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	–2.01	–0.04

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 410, Method 418A and 418B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1426–74, Method A, p 237 (1976).

EPA METHOD
NO. 350.3

NITROGEN, AMMONIA

Method 350.3 (Potentiometric, Ion Selective Electrode)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
   1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 This method covers the range from 0.03 to 1400 mg NH_3–N/1. Color and turbidity have no effect on the measurements, thus, distillation may not be necessary.
2. Summary of Method
   2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
   2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
   4.1 Volatile amines act as a positive interference.
   4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.
5. Apparatus
   5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.
   5.2 Ammonia selective electrode, such as Orion Model 95–10 or EIL Model 8002–2.
   5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
6. Reagents
   6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.
   6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 ml of distilled water. Cool and dilute to 1 liter with distilled water (6.1).
   6.3 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

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6.4 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3–N. Dilute 10.0 ml of the stock solution (6.3) to 1 liter with distilled water (6.1) in a volumetric flask.

NOTE 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350.1).

7. Procedure

7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

7.2 Calibration of electrometer: Place 100 ml of each standard solution in clean 150 ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

NOTE 2: The pH of the solution after the addition of NaOH must be above 11.

Caution: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH_3–N/1 on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 ml of sample in 150 ml beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg NH_3–N/1.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH_3–N/1, standard deviations were ±0.038, ±0.017, ±0.007, and ±0.003, respectively.

8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg NH_3–N/1, recoveries were 96% and 91%, respectively.

Bibliography

1. Booth, R. L., and Thomas, R. F., "Selective Electrode Determination of Ammonia in Water and Wastes", Envir. Sci. Technology, 7, p 523–526 (1973).
2. Banwart, W. L., Bremner, J. M., and Tabatabai, M. A., "Determination of Ammonium in Soil Extracts and Water Samples by an Ammonia Electrode", Comm. Soil Sci. Plant.,3,p 449 (1952).
3. Midgley, D., and Torrance, K., "The Determination of Ammonia in Condensed Steam and Boiler Feed-Water with a Potentiometric Ammonia Probe", Analyst, 97 p 626–633 (1972).

EPA METHOD
NO. 405.1

BIOCHEMICAL OXYGEN DEMAND

Method 405.1 (5 Days, 20°C)

STORET NO. 00310
Carbonaceous 80082

and Application

The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

ary of Method

he sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

ents

Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.

Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (also found in this manual).

he use of 60 ml incubation bottles in place of the usual 300 ml incubation bottles, in conjunction with the probe, is often convenient.

on and Accuracy

ighty-six analysts in fifty-eight laboratories analyzed natural water samples plus an xact increment of biodegradable organic compounds. At a mean value of 2.1 and 175 ng/l BOD, the standard deviation was ±0.7 and ±26 mg/l, respectively (EPA Method esearch Study 3).

here is no acceptable procedure for determining the accuracy of the BOD test.

NPDES (CBOD: pending approval for Section 301(h), CWA)

ision 1974

5. References

5.1 The procedure to be used for this determination is found in:
Standard Methods for the Examination of Water and Wastewater, 15th Edition, p. 483, Method 507 (1980).

5.2 Young, J. C., "Chemical Methods for Nitrification Control," J. Water Poll. Control Fed., 45, p. 637 (1973).

EPA METHOD
NO. 300

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

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EPA

Test Method

The Determination of Inorganic Anions in Water by Ion Chromatography — Method 300.0

James W. O'Dell, John D. Pfaff, Morris E. Gales, and Gerald D. McKee

1. Scope and Application

1.1 This method covers the determination of the following inorganic anions.

	Storet No.	
Analyte	Total	Dissolved
Chloride	00940	—
Fluoride	00951	00950
Nitrate-N	00620	—
Nitrite-N	00615	—
Ortho-Phosphate-P	—	00671
Sulfate	00945	—

1.2 This is an ion chromatographic (IC) method applicable to the determination of the anions listed above in drinking water, surface water, and mixed domestic and industrial wastewater.

1.3 The Method Detection Limit (MDL, defined in Section 13) for the above analytes is listed in Table 1. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 10.2.

1.5 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the addition of spike solutions covering the anions of interest. The spike procedure is described in Section 11.6.

2. Summary of Method

2.1 A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor column, and conductivity detector.

3. Definitions

3.1 Stock standard solution — a concentrated solution containing a certified standard that is a method analyte. Stock standard solutions are used to prepare secondary standard solutions.

3.2 Calibration standards — a solution of analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare aqueous calibration solutions.

3.3 Quality control check sample — a solution containing known concentrations of analytes, prepared by a laboratory other than the laboratory performing the analysis. The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

3.4 Performance evaluation sample — a solution of method analytes distributed by the Quality Assurance Branch (QAB), Environmental Monitoring and Support Laboratory (EMSL-Cincinnati), USEPA, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by the QAB to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.5 Laboratory control standards — a solution of analytes prepared in the laboratory by adding appropriate volumes of the stock standard solutions to reagent water.

3.6 Laboratory duplicates — two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

3.7 Field duplicates — two samples taken at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

4. Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

4.2 The water dip or negative peak that elutes near and can interfere with the fluoride peak can be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

5. Safety

5.1 Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method.

6. Apparatus and Materials

6.1 Balance — Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Ion chromatograph — Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed air, detector, and stripchart recorder. A data system is recommended for peak integration.

6.2.1 Anion guard column: 4 x 50 mm, Dionex P/N 030825, or equivalent.

6.2.2 Anion separator column: 4 x 250 mm, Dionex P/N 030827, or equivalent.

6.2.3 Anion suppressor column: fiber, Dionex P/N 35350, or equivalent.

6.2.4 Detector — Conductivity cell: approximately 6 μL volume, Dionex, or equivalent.

7. Reagents and Consumable Materials

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution: Sodium bicarbonate (CAS RN 144-55-8) 0.003 M, sodium carbonate (CAS RN 497-19-8) 0.0024M. Dissolve 1.0081 g sodium bicarbonate ($NaHCO_3$) and 1.0176 g of sodium carbonate (Na_2CO_3) in reagent water and dilute to 4 liters.

7.4 Regeneration solution (fiber suppressor): Sulfuric acid (CAS RN 7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 liters with reagent water.

7.5 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min.) as listed below.

7.5.1 Chloride (CL^-) 1000 mg/L: Dissolve 1.6485 g sodium chloride (NaCL, CAS RN 7647-14-5) in reagent water and dilute to 1 liter.

7.5.2 Fluoride (F^-) 1000 mg/L: Dissolve 2.2100 g sodium fluoride (NaF, CAS RN 7681-49-4) in reagent water and dilute to 1 liter.

7.5.3 Nitrate (NO_3^--N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate ($NaNO_3$, CAS RN 7631-99-4) in reagent water and dilute to 1 liter.

7.5.4 Nitrite (NO_2^--N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite ($NaNO_2$, CAS RN 7632-00-0) in reagent water and dilute to 1 liter.

7.5.5 Phosphate ($PO_4^{\equiv}$-P) 1000 mg/L: Dissolve 4.3937 g potassium phosphate (KH_2PO_4, CAS RN 7778-77-0) in reagent water and dilute to 1 liter.

7.5.6 Sulfate ($SO_4^{=}$) 1000 mg/L: Dissolve 1.8141 g potassium sulfate (K_2SO_4, CAS RN 7778-80-5) in reagent water and dilute to 1 liter.

7.5.7 Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

8. Sample Collection, Preservation and Storage

8.1 Samples should be collected in scrupulously clean glass or polyethylene bottles.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follows:

Analyte	Preservation	Holding Time
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
O-Phosphate-P	Filter and cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment and holding time for the total sample.

9. Calibration and Standardization

9.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

9.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (7.5) to a volumetric flask and diluting to volume with reagent water. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

9.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. The retention time is inversely proportional to the concentration.

9.4 The working calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ± 10%, the test must be repeated, using fresh calibration standards. If the results are still more than ± 10%, an entire new calibration curve must be prepared for that analyte.

9.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (all anions) should not exceed about 400 ppm.

10. Quality Control

10.1 Each laboratory using this method should have a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (10.2) and the analysis of spiked samples as a continuing check on performance. The laboratory should maintain performance records to define the quality of data that are generated.

10.1.1 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.1.2 The laboratory should spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. Field and laboratory duplicates should also be analyzed.

10.2 Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision with this method, using a laboratory control standard.

10.2.1 Select a representative spike concentration for each analyte to be measured. Using stock standards, prepare a quality control check sample concentrate in reagent water 100 times more concentrated than the selected concentrations.

10.2.2 Using a pipet, add 1.00 mL of the check sample concentrate (10.2.1) to each of a minimum of four 100-mL aliquots of reagent water. Analyze the aliquots according to the procedure in Section 11.

10.2.3 Calculate the average percent recovery (R), and the standard deviation(s) of the percent recovery, for the results.

10.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values calculated in Section 10.2.3. If the data are not comparable within control limits (10.3.1), review potential problem areas and repeat the test.

10.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration of analyte being measured.

10.3.1 Calculate upper and lower control limits for method performance as follows:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

where R and s are calculated as in Section 10.2.3. The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

10.4 The laboratory should develop and maintain separate accuracy statements of laboratory performance for water and wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analyses of four aliquots of water or wastewater, as described in Section 10.2.2, followed by the calculation of R and s.

10.5 Before processing any samples, the analyst must demonstrate through the analysis of an aliquot of reagent water that all glassware and reagent interferences are under control. Each time there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

10.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and spiking, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

11. Procedure

11.1 Table 1 summarizes the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 9.

11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, spike the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can produce poor resolution or misidentification.

12. Calculation

12.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

12.2 Report results in mg/L.

13. Precision and Accuracy — Method Detection Limit

13.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water.

13.2 Single-operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 2.

14. References

14.1 Annual Book of ASTM Standards, Part 31 Water, proposed test method for "Anions in Water by Ion Chromatography," p. 1485-1492 (1982).

14.2 Standard Methods for the Examination of Water and Wastewater, Method 400Z, "Anions by Ion Chromatography" proposed for the 16th Edition of Standard Methods.

14.3 Dionex, IC 16 operation and maintenance manual, PN 30579, Dionex Corp., Sunnyvale, California 94086.

14.4 Method detection limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, *Environmental Science and Technology*, Vol. 15, Number 12, p. 1426, December 1981.

Table 1. Chromatographic Conditions and Method Detection Limits in Reagent Water

Analyte	Retention[1] Time (Min)	Relative Retention Time	Method[2] Detection Limit mg/L
Fluoride	1.2	1.0	0.005
Chloride	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004
O-Phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulfate	21.4	17.8	0.206

Standard Conditions:

Columns — As specified in 6.2 Sample Loop — 100 µL
Detector — As specified in 6.2 Pump Volume — 2.30 mL/Min
Eluent — As specified in 7.3

[1] Concentrations of mixed standard (mg/L)
Fluoride 3.0 O-Phosphate-P 9.0
Chloride 4.0 Nitrate-N 30.0
Nitrite-N 10.0 Sulfate 50.0

[2] MDL calculated from data obtained using an attenuator setting of 1 µMHO full scale. Other settings would produce an MDL proportional to their value.

Table 2. Single-Operator Accuracy and Precision

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Chloride	RW	0.050	7	97.7	0.0047
	DW	10.0	7	98.2	0.289
	SW	1.0	7	105.0	0.139
	WW	7.5	7	82.7	0.445
Fluoride	RW	0.24	7	103.1	0.0009
	DW	9.3	7	87.7	0.075
	SW	0.50	7	74.0	0.0038
	WW	1.0	7	92.0	0.011
Nitrate-N	RW	0.10	7	100.9	0.0041
	DW	31.0	7	100.7	0.356
	SW	0.50	7	100.0	0.0058
	WW	4.0	7	94.3	0.058
Nitrite-N	RW	0.10	7	97.7	0.0014
	DW	19.6	7	103.3	0.150
	SW	0.51	7	88.2	0.0053
	WW	0.52	7	100.0	0.018
O-Phosphate-P	RW	0.50	7	100.4	0.019
	DW	45.7	7	102.5	0.386
	SW	0.51	7	94.1	0.020
	WW	4.0	7	97.3	0.04
Sulfate	RW	1.02	7	102.1	0.066
	DW	98.5	7	104.3	1.475
	SW	10.0	7	111.6	0.709
	WW	12.5	7	134.9	0.466

RW = Reagent Water SW = Surface Water
DW = Drinking Water WW = Wastewater

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FREE CHLORINE
(FIELD DETERMINATION)

FREE CHLORINE

Liquid samples were tested in the field for free chlorine content prior to the addition of any preservatives. This was done to determine whether a VOA vial preserved with sodium thiosulfate was necessary. Free chlorine tests were conducted using a chlorine test kit made by Coastal Chemical Company. The kit is equiped with a cell in which to place the test sample, a color chart to compare the sample with, and a small bottle of orthotolidine. The color chart ranges from pale yellow (0.2 ppm chlorine) to bright yellow (1.0 ppm chlorine). The chart measures color changes corresponding to quantities of 0.2, 0.4, 0.6, 0.8, and 1.0 ppm chlorine. Intermediate chlorine levels can be estimated.

To test for free chlorine, liquid is placed in the test cell up to a measured limit. Four drops of orthotolidine are added and the cell contents are mixed. Any color change is compared to the color chart.

EPA METHOD
NO. 410.4M

CHEMICAL OXYGEN DEMAND

Method 410.4 (Colorimetric, Automated; Manual)

STORET NO. 00340

1. Scope and Application
   - 1.1 This method covers the determination of COD in surface waters, domestic and industrial wastes.
   - 1.2 The applicable range of the automated method is 3–900 mg/1 and the range of the manual method is 20 to 900 mg/1.
2. Summary of Method
   - 2.1 Sample, blanks and standards in sealed tubes are heated in an oven or block digestor in the presence of dichromate at 150°C. After two hours, the tubes are removed from the oven or digestor, cooled and measured spectrophotometrically at 600 nm.
3. Sample Handling and Preservation
   - 3.1 Collect the samples in glass bottles if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
   - 3.2 Samples should be preserved with sulfuric acid to a $pH < 2$ and maintained at 4°C until analysis.
4. Interferences
   - 4.1 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.
5. Apparatus
   - 5.1 Drying oven or block digestor, 150°C
   - 5.2 Corning culture tubes, 16 x 100 mm or 25 x 150 mm with Teflon lined screw cap
   - 5.3 Spectrophotometer or Technicon AutoAnalyzer
   - 5.4 Muffle furnace, 500°C.
6. Reagents
   - 6.1 Digestion solution: Add 10.2 g $K_2Cr_2O_7$, 167 ml conc. H_2SO_4 and 33.3 g $HgSO_4$ to 500 ml of distilled water, cool and dilute to 1 liter.
   - 6.2 Catalyst solution: Add 22 g Ag_2SO_4 to a 4.09kg bottle of conc. H_2SO_4. Stir until dissolved.
   - 6.3 Sampler wash solution: Add 500 ml of conc H_2SO_4 to 500 ml of distilled water.
   - 6.4 Stock potassium acid phthalate: Dissolve 0.850 g in 800 ml of distilled water and dilute to 1 liter. 1 ml = 1 mg COD
     - 6.4.1 Prepare a series of standard solutions that cover the expected sample concentrations by diluting appropriate volumes of the stock standard.
7. Procedure
   - 7.1 Wash all culture tubes and screw caps with 20% H_2SO_4 before their first use to prevent contamination. Trace contamination may be removed from the tubes by igniting them in a muffle oven at 500°C for 1 hour.

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7.2 Automated
    7.2.1 Add 2.5 ml of sample to the 16 x 100 mm tubes.
    7.2.2 Add 1.5 ml of digestion solution (6.1) and mix.
    7.2.3 Add 3.5 ml of catalyst solution (6.2) carefully down the side of the culture tube.
    7.2.4 Cap tightly and shake to mix layers.
    7.2.5 Process standards and blanks exactly as the samples.
    7.2.6 Place in oven or block digestor at 150°C for two hours.
    7.2.7 Cool, and place standards in sampler in order of decreasing concentration. Complete filling sampler tray with unknown samples.
    7.2.8 Measure color intensity on AutoAnalyzer at 600 nm.

7.3 Manual
    7.3.1 The following procedure may be used if a larger sample is desired or a spectrophotometer is used in place of an AutoAnalyzer.
    7.3.2 Add 10 ml of sample to 25 x 150 mm culture tube.
    7.3.3 Add 6 ml of digestion solution (6.1) and mix.
    7.3.4 Add 14 ml of catalyst solution (6.2) down the side of culture tube.
    7.3.5 Cap tightly and shake to mix layers.
    7.3.6 Place in oven or block digestor at 150°C for 2 hours.
    7.3.7 Cool, allow any precipitate to settle and measure intensity in spectrophotometer at 600 nm. Use only optically matched culture tubes or a single cell for spectrophotometric measurement.

8. Calculation
    8.1 Prepare a standard curve by plotting peak height or percent transmittance against known concentrations of standards.
    8.2 Compute concentration of samples by comparing sample response to standard curve.

9. Precision and Accuracy
    9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Jirka, A. M., and M. J. Carter, "Micro-Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand." Anal. Chem. 47:1397. (1975).

EPA METHOD
NO. 335.2

CYANIDE, TOTAL

Method 335.2 (Titrimetric; Spectrophotometric)

STORET NO. 00720

1. Scope and Application

   1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.

   1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/1 (0.25 mg/250 ml of absorbing liquid).

   1.3 The colorimetric procedure is used for concentrations below 1 mg/1 of cyanide and is sensitive to about 0.02 mg/1.

2. Summary of Method

   2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

   2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

   2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

   3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

   4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

   4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

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4.3 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH ≥ 12) at the time of collection.

4.4 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1, 8.2 and 8.3.

5.2 Sulfides adversely affect the colorimetric and titration procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the optional procedure described in Procedure 8.2. The apparatus for this procedure is shown in Figure 3.

5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.

5.3.1 Acidify the sample with acetic acid (1 + 9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

5.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid which will react with some organic compounds to form oximes. These compounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 Reflux distillation apparatus for sulfide removal as shown in Figure 3. The boiling flask same as 6.1. The sulfide scrubber may be a Wheaton Bubber #709682 with 29/42 joints, size 100 ml. The air inlet tube should not be fritted. The cyanide absorption vessel should be the same as the sulfide scrubber. The air inlet tube should be fritted.

6.5 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-164-50).

7. Reagents

7.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.2 Lead acetate: Dissolve 30 g of $Pb(C_2H_3O_2) \cdot 3H_2O$ in 950 ml of distilled water. Adjust the pH to 4.5 with acetic acid. Dilute to 1 liter.

7.5 Sulfuric acid; 18N: Slowly add 500 ml of concentrated H_2SO_4 to 500 ml of distilled water.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 100.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 100.0 ug).

7.9 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 10.0 ug CN.

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = 1mg CN).

7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.

7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh daily.

7.13 Color Reagent — One of the following may be used:

7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl, mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'Dimethyl-1, 1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.14 Magnesium chloride solution: Weight 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.

7.15 Sulfamic acid.

8. Procedure

8.1 For samples without sulfide.

8.1.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap in the train. (Figure 1 or 2)

8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enters the boiling flask through the air inlet tube. Proceed to 8.4.

8.2 For samples that contain sulfide.

8.2.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) to the absorbing tube. Add 25 ml of lead acetate (7.2) to the sulfide scrubber. Connect the boiling flask, condenser, scrubber and absorber in the train. (Figure 3) The flow meter is connected to the outlet tube of the cyanide absorber.

8.2.2 Start a stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1.5 liters per minute enters the boiling flask through the air inlet tube. The bubble rate may not remain constant while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally. Proceed to 8.4.

8.3 If samples contain NO_3 and or NO_2 add 2 g of sulfamic acid solution (7.15) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

8.4 Slowly add 50 ml 18N sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 20 ml of magnesium chloride (7.14) into the air inlet and wash down with a stream of water.

8.5 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.6 Drain the solution from the absorber into a 250 ml volumetric flask. Wash the absorber with distilled water and add the washings to the flask. Dilute to the mark with distilled water.

8.7 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25N sodium hydroxide solution (7.4). Add 15.0 ml of sodium phosphate solution (7.6) and mix.

8.7.1 Pyridine-barbituric acid method: Add 2 ml of chloramine T (7.12) and mix. See Note 1. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.7.2 Pyridine-pyrazolene method: Add 0.5 ml of chloramine T (7.12) and mix. See Note 1 and 2. After 1 to 2 minutes add 5 ml of pyridine-pyrazolone solution

(7.13.1) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

NOTE 1: Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 ml of chlorine T. After one minute, recheck the sample.

NOTE 2: More than 05. ml of chloramine T will prevent the color from developing with pyridine-pyrazolone.

8.8 Standard curve for samples without sulfide.

8.8.1 Prepare a series of standards by pipeting suitable volumes of standard solution (7.9) into 250 ml volumetric flasks. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Prepare as follows:

ML of Working Standard Solution (1 ml = 10 μg CN)	Conc. μg CN per 250 ml
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

8.8.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that,at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards the analyst should find the cause of the apparent error before proceeding.

8.8.3 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to 500 ml of sample to insure a level of 20 μg/l. Proceed with the analysis as in Procedure (8.1.1).

8.9 Standard curve for samples with sulfide.

8.9.1 It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increases, the recovery decreases. It is recommended that at least 3 standards be distilled.

8.9.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.10 Titrimetric method.

8.10.1 If the sample contains more than 1 mg/l of CN, transfer the distillate or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.10.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.10.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples.

9. Calculation

9.1 If the colorimetric procedure is used, calculate the cyanide, in ug/l, in the original sample as follows:

$$\text{CN}, ug/l = \frac{A \times 1{,}000}{B} \times \frac{50}{C}$$

where:

A = ug CN read from standard curve
B = ml of original sample for distillation
C = ml taken for colorimetric analysis

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A - B)1{,}000}{\text{ml orig. sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.
B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy

10.1 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/l CN, the standard deviations were ±0.005, ±0.007, ±0.031 and ±0.094, respectively.

10.2 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/l CN, recoveries were 85% and 102%, respectively.

Bibliography

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2. Elly, C. T. "Recovery of Cyanides by Modified Serfass Distillation". Journal Water Pollution Control Federation 40:848–856 (1968).
3. Annual Book of ASTM Standards, Part 31, "Water", Standard D2036–75, Method A, p 503 (1976).
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5. Egekeze, J. O., and Oehne, F. W., "Direct Potentiometric Determination of Cyanide in Biological Materials," J. Analytical Toxicology, Vol. 3, p. 119, May/June 1979.
6. Casey, J. P., Bright, J. W., and Helms, B. D., "Nitrosation Interference in Distillation Tests for Cyanide," Gulf Coast Waste Disposal Authority, Houston, Texas.

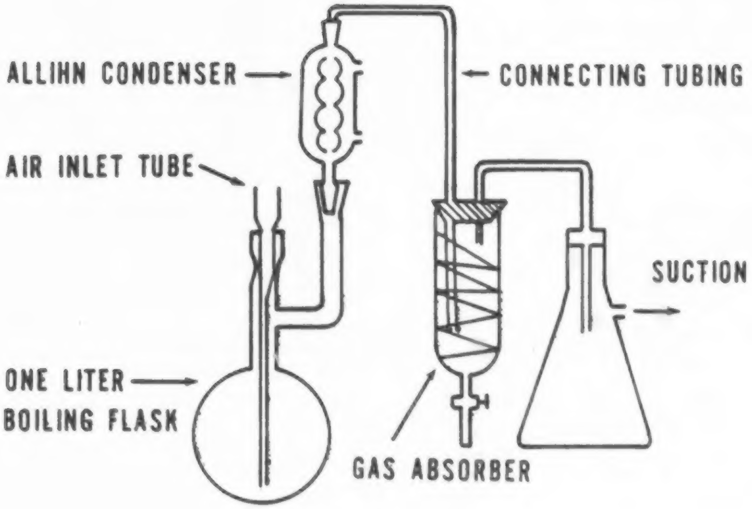
ALLIHN CONDENSER
CONNECTING TUBING
AIR INLET TUBE
SUCTION
ONE LITER
BOILING FLASK
GAS ABSORBER

FIGURE 1

CYANIDE DISTILLATION APPARATUS

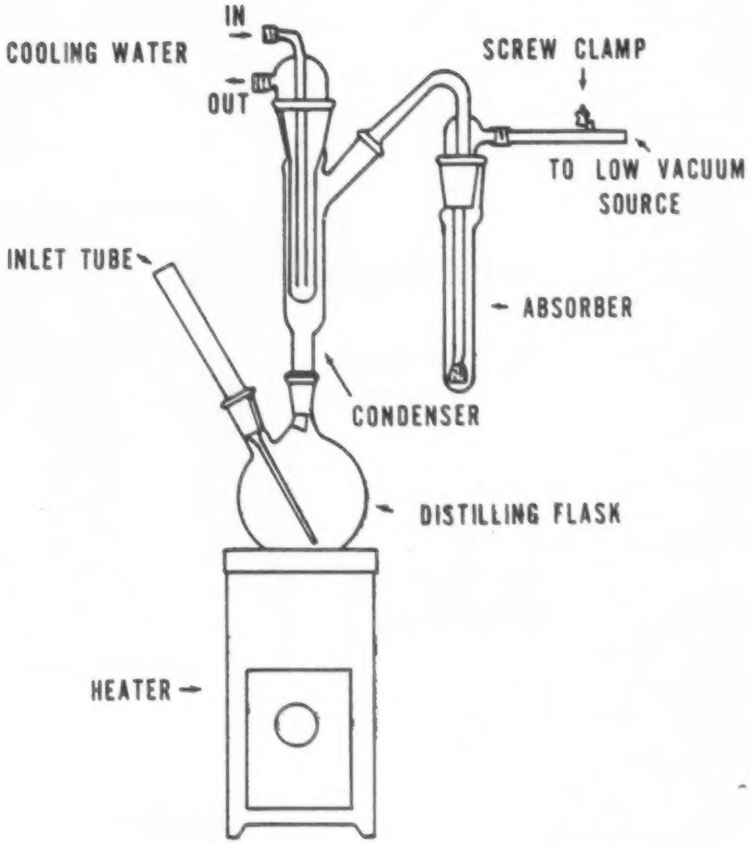
IN
COOLING WATER
OUT
SCREW CLAMP
TO LOW VACUUM SOURCE
INLET TUBE
ABSORBER
CONDENSER
DISTILLING FLASK
HEATER

FIGURE 2

CYANIDE DISTILLATION APPARATUS

EPA METHOD
NO. 340.1

FLUORIDE, TOTAL

Method 340.1 (Colorimetric, SPADNS with Bellack Distillation)

STORET NO. Total 00951
Dissolved 00950

1. Scope and Application
   1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The method covers the range from 0.1 to about 2.5 mg/1 F. This range may be extended to 1000 mg/1 using the Fluoride Ion Selective Electrode Method (340.2) after distillation.
2. Summary of Method
   2.1 Following distillation to remove interferences, the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.
3. Comments
   3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 414:1, p 388, Standard Methods for the Examination of Waters and Wastewaters, 14th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent additon is the most prominent source of error in this test.
   3.2 Care must be taken to avoid overheating the flask above the level of the solution. This is done by maintaining an even flame entirely under the boiling flask.
4. Apparatus
   4.1 Distillation apparatus: A 1-liter round-bottom, long-necked pyrex boiling flask, connecting tube, efficient condenser, thermometer adapter and thermometer reading to 200°C. All connections should be ground glass. Any apparatus equivalent to that shown in Figure 1 is acceptable.
   4.2 Colorimeter: One of the following
      4.2.1 Spectrophotometer for use at 570 nm providing a light path of at least 1 cm.
      4.2.2 Filter photometer equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm and a light path of at least 1 cm.
5. Reagents
   5.1 Sulfuric acid, H_2SO_4, conc.

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5.2 Silver sulfate Ag_2SO_4 crystals.

5.3 Stock fluoride solution: Dissolve 0.221 g anhydrous sodium fluoride, NaF, in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.1 mg F.

5.4 Standard fluoride solution: Place 100 ml stock fluoride solution (5.3) in a 1 liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.010 mg F.

5.5 SPADNS solution: Dissolve 0.958 g SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, in distilled water in a 500 ml volumetric flask and dilute to the mark. Stable indefinitely if protected from direct sunlight.

5.6 Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate, $Zr0Cl_2 \cdot 8H_2O$ in approximately 25 ml distilled water in a 500 ml volumetric flask. Add 350 ml conc HCl and dilute to the mark with distilled water.

5.7 Acid-zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution (5.5) and zirconyl-acid reagent (5.6). The combined reagent is stable for at least 2 years.

5.8 Reference solution: Add 10 ml SPADNS solution (5.5) to 100 ml distilled water. Dilute 7 ml conc HCl to 10 ml and add to the dilute SPADNS solution. This solution is used for zeroing the spectrophotometer or photometer. It is stable and may be used indefinitely.

5.9 Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water (CAUTION: Toxic-avoid ingestion).

6. Procedure

6.1 Preliminary distillation

6.1.1 Place 400 ml distilled water in the distilling flask.

6.1.2 Carefully add 200 ml cono. H_2SO_4 and swirl until contents are homogeneous.

6.1.3 Add 25 to 35 glass beads, connect the apparatus (Figure 1) making sure all joints are tight.

6.1.4 Heat slowly at first, then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until the temperature of the flask contents reaches exactly 180°C. Discard the distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.

6.1.5 Cool to 120°C or below.

6.1.6 Add 300 ml sample, mix thoroughly, distill as in 6.1.4 until temperature reaches 180°C. Do not heat above 180°C to prevent sulfate carryover.

6.1.7 Add Ag_2SO_4 (5.2) at a rate of 5 mg/mg Cl when high chloride samples are distilled.

6.1.8 Use the sulfuric acid solution in the flask repeatedly until the contaminants from the samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.

6.1.9 High fluoride samples may require that the still be flushed by using distilled water and combining distillates.

6.2 Colorimetric Determination:

6.2.1 Prepare fluoride standards in the range 0 to 1.40 mg/l by diluting appropriate quantities of standard fluoride solution (5.4) to 50 ml with distilled water.

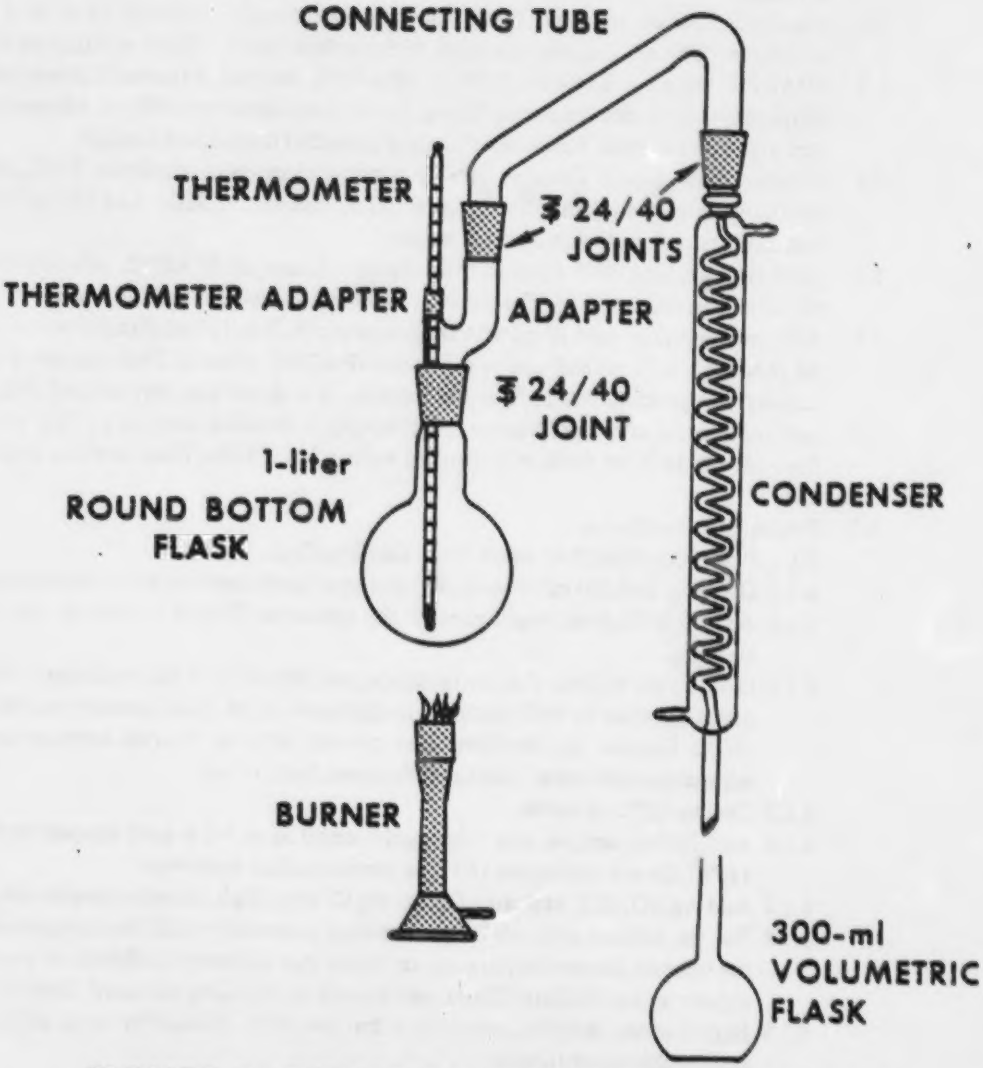
CONNECTING TUBE
THERMOMETER
₮ 24/40
JOINTS
THERMOMETER ADAPTER
ADAPTER
₮ 24/40
JOINT
1-liter
ROUND BOTTOM
FLASK
CONDENSER
BURNER
300-ml
VOLUMETRIC
FLASK

FIGURE 1 DIRECT DISTILLATION APPARATUS FOR FLUORIDE.

6.2.2 Pipet 5.00 ml each of SPADNS solution (5.5) and zirconyl-acid reagent (5.6) or 10.00 ml of the mixed acid-zirconyl-SPADNS reagent (5.7) to each standard and mix well.

6.2.3 Set photometer to zero with reference solution (5.8) and immediately obtain absorbance readings of standards.

6.2.4 Plot absorbance versus concentration. Prepare a new standard curve whenever fresh reagent is made.

6.2.5 If residual chlorine is present pretreat the sample with 1 drop (0.05 ml) $NaAsO_2$ solution (5.9) per 0.1 mg residual chlorine and mix. Sodium arsenite concentrations of 1300 mg/1 produce an error of 0.1 mg/1 at 1.0 mg/1 F.

6.2.6 Use a 50 ml sample or a portion diluted to 50 ml. Adjust the temperature of the sample to that used for the standard curve.

6.2.7 Perform step 6.2.2 and 6.2.3.

7. Calculations

7.1 Read the concentration in the 50 ml sample using the standard curve (6.2.4)

7.2 Calculate as follows:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}}$$

7.3 When a sample (ml sample) is diluted to [illegible] (B) and then a portion (C) is analyzed, use:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}} \times \frac{B}{C}$$

8. Precision and Accuracy

8.1 On a sample containing 0.83 mg/1 F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/1 F with a standard deviation of ±0.089 mg/1.

8.2 On a sample containing 0.57 mg/1 F (with 200 mg/1 SO_4 and 10 mg/1 Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg/1F with a standard deviation of ±0.103 mg/1.

8.3 On a sample containing 0.68 mg/1 F (with 200 mg/1 SO_4, 2 mg/1 Al and 2.5 mg/1 $[Na(PO_3)_6]$ as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/1 F with a standard deviation of ±0.092 mg/1. (Analytical Reference Service, Sample 111-B water, Fluoride, August, 1961.)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p. 389–390 (Method No. 414A, Preliminary Distillation Step) and p. 393–394 (Method 414C SPADNS) 14th Edition, (1975).

2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1179–72, Method A, p. 310 (1976).

pH
(FIELD DETERMINATION)

pH

Liquid and sludge samples were tested for pH in the field prior to the addition of any preservatives. Values of pH were measured using "Alkacid Test Ribbon" manufactured by Fischer Scientific Company. This pH paper provides 5 distinct color changes ranging from violet (pH = 2) to dark blue (pH = 10). A color comparison chart is included with the paper. The chart indicates the colors for pH values of 2, 4, 6, 8, and 10. Intermediate pH values can be estimated.

To determine the pH a liquid sample, a section of the pH ribbon is removed from the dispenser and a small amount of liquid (a few drops) is applied to the paper. Any color change will occur immediately and is compared to the color chart while the paper is still wet. To determine the pH of a sludge sample, a small amount of sludge is applied to the paper. Time is allowed for the fluid content of the sludge to absorb into the pH ribbon. Once this has occurred, any color change is compared to the chart.

EPA METHOD
NO. 150.1

pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
   4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

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5.2 Glass electrode.

5.3 Reference electrode–a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (<0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

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[1] National Bureau of Standards Special Publication 260.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Bias, pH Units
3.5	0.10	−0.29	−0.01
3.5	0.11	−0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	−0.03	−0.002
8.0	0.13	−0.12	−0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293–65, p 178 (1976).

EPA METHOD
NO. 413.1

OIL AND GREASE, TOTAL, RECOVERABLE

Method 413.1 (Gravimetric, Separatory Funnel Extraction)

STORET NO. 00556

1. Scope and Application
   - 1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
   - 1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation.
   - 1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.
   - 1.4 The method covers the range from 5 to 1000 mg/1 of extractable material.
2. Summary of Method
   - 2.1 The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.
3. Definitions
   - 3.1 The definition of oil and grease is based on the procedure used. The nature of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.
4. Sampling and Storage
   - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.
   - 4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.
5. Apparatus
   - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   - 5.2 Vacuum pump, or other source of vacuum.
   - 5.3 Flask, boiling, 125 ml (Corning No. 4100 or equivalent).
   - 5.4 Distilling head, Claisen or equivalent.
   - 5.5 Filter paper, Whatman No. 40, 11 cm.
6. Reagents
   - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.

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6.2 Flurocarbon-113,(1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Tare a boiling flask (pre-dried in an oven at 103°C and stored in a desiccator).

7.4 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate, and filter the solvent layer into the flask through a funnel containing solvent moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.4) twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.

7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10–20 ml solvent and collect the rinsings in the flask.

7.7 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each set of samples.

7.8 When the temperature in the distilling head reaches 50°C or the flask appears dry remove the distilling head. Sweep out the flask for 15 seconds with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.

7.9 Cool the boiling flask in a desiccator for 30 minutes and weigh.

8. Calculation

8.1 mg/l total oil and grease = $\frac{R - B}{V}$

where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams.

B = blank determination, residue of equivalent volume of extraction solvent, in milligrams.

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 12.6 mg/1. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 93% with a standard deviation of ±0.9 mg/1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 515, Method 502A, (1975).
2. Blum, K. A., and Taras, M. J., "Determination of Emulsifying Oil in Industrial Wastewater", JWPCF Research Suppl. 40, R404 (1968).

OIL AND GREASE ANALYSIS OF SLUDGE SAMPLES
-RETORT METHOD-

Oil and Grease Analysis of Sludge Samples

A study was performed to determine a quick, reliable method for the determination of oil and grease in sludge samples. Oil and grease is defined to mean that material which can be extracted from the sample by freon extraction and which is determined by gravimetry after evaporating the freon from sodium sulfate dried extract. Three methods were compared: the straight freon extraction method (A); the sonication assisted freon extraction method (B) and the freon extraction following retort (C). A brief description of each method will be given below.

Method A: A weighed aliquot (approximately 10 grams) of well mixed sludge is acidified to pH 2 by addition a few drops of dilute HCl. The sample is extracted by shaking with three successive portions (30 mL each) of freon. The extracts are dried by passing them through anhydrous sodium sulfate contained in a filter tube plugged with glass wool. The sodium sulfate is rinsed with an additional aliquot of clean freon which is then combined with the extracts. The freon is then removed by evaporation over a steam bath and the oil and grease residue is determined by gravimetric analysis.

Method B: Method B is identical to Method A except that the extraction is assisted by sonicating the freon and sludge to attempt to get a better recovery of oil and grease.

Method C: A weighed aliquot (approximately 20 grams) of well mixed sludge is acidified to pH 2 by addition of a few drops of dilute HCl. The sample is then placed in a retort apparatus. The sample is heated from ambient to approximately 500 degrees centigrade over 30 minutes. The distillate is condensed and collected in a side arm receiver. The oil and grease is determined in the distillate by the procedure outlined in Method A.

The results of this study suggest that the retort step (Method C) yields a higher oil and grease result with considerably less variability than either Methods A or B. The sonication step (Method B) actually yielded a lower oil and grease result than either Methods A or C. This was contrary to our expectations, however, there was no specific attempt to discover the reason for the lower results.

The results of this study are presented graphically in figures 1 and 2. Two actual field samples were used. One was considered to have a moderate oil and grease value and the other a high value.

K•E 10 X 10 TO ½ INCH 7 X 10 INCHES KEUFFEL & ESSER CO. MADE IN U.S.A.

46 1320

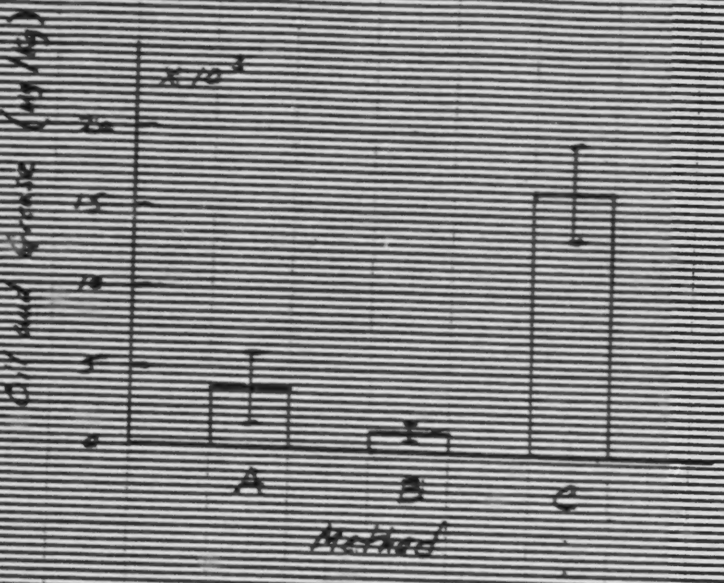

Figure 1. Oil and Grease analysis comparison of Methods A, B and C (see text) for sludge sample with moderate oil and grease content. The error bar depicts the variability of duplicate analyses by each method.

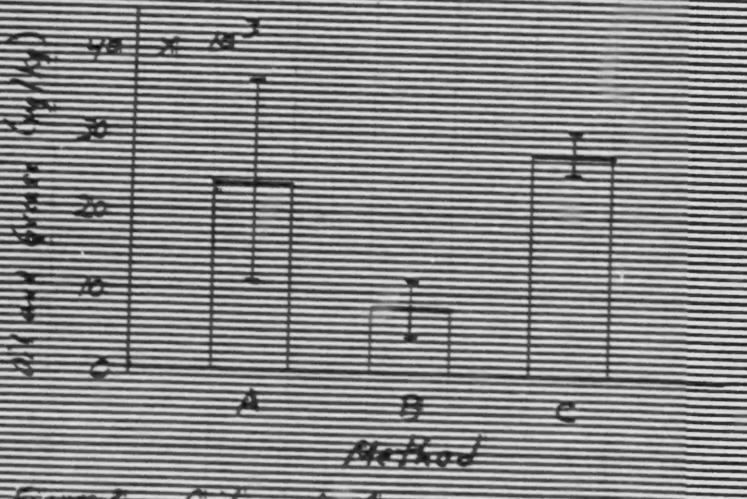

Figure 2. Oil and Grease analysis Comparison of Methods A, B and C (see text) for a sludge sample with high oil and grease content. The error bar depicts the variability of duplicate analyses by each method.

EPA METHOD
NO. 160.1

RESIDUE, FILTERABLE

Method 160.1 (Gravimetric, Dried at 180°C)

STORET NO. 70300

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The practical range of the determination is 10 mg/l to 20,000 mg/l.
2. Summary of Method
   2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
   2.2 If Residue, Non-Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.
3. Definitions
   3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.
4. Sample Handling and Preservation
   4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
   5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
   5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.
6. Apparatus
   6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent.
   6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.
   6.3 Suction flask, 500 ml.
   6.4 Gooch crucibles, 25 ml (if 2.1 cm filter is used).
   6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).
   6.6 Steam bath.
   6.7 Drying oven, 180°C ±2°C.
   6.8 Desiccator.

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Issued 1971

6.9 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to 550 ±50°C for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to 180 ±2°C for one hour. Cool in desiccator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If total filterable residue is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter, rinse with three 10 ml portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180 ±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8. Calculation

8.1 Calculate filterable residue as follows:

$$\text{Filterable residue, mg/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in ml

9. Precision and Accuracy

9.1 Precision and accuracy are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

EPA METHOD
NO. 160.2

RESIDUE, NON-FILTERABLE

Method 160.2 (Gravimetric, Dried at 103–105°C)

STORET NO. 00530

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The practical range of the determination is 4 mg/1 to 20,000 mg/1.
2. Summary of Method
   2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103–105°C.
   2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
   3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103–105°C.
4. Sample Handling and Preservation
   4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
   5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.
6. Apparatus
   6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.
   NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
   6.2 Filter support: filtering apparatus with reservoir and a coarse (40–60 microns) fritted disc as a filter support.

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NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

6.3 Suction flask.

6.4 Drying oven, 103–105°C.

6.5 Desiccator.

6.6 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103–105°C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of Sample Volume

For a 4.7 cm diameter filter, filter 100 ml of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 ml/cm^2 of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

NOTE: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five ml increments for timing are suggested. Continue to record the time and volume increments until fitration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

NOTE: Total volume of wash water used should equal approximately 2 ml per cm^2. For a 4.7 cm filter the total volume is 30 ml.

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103–105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8. Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A - B)\times 1{,}000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = ml of sample filtered

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

EPA METHOD
NO. 160.3

RESIDUE, TOTAL

Method 160.3 (Gravimetric, Dried at 103–105°C)

STORET NO. 00500

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is from 10 mg/l to 20,000 mg/l.
2. Summary of Method
   - 2.1 A well mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103–105°C.
3. Definitions
   - 3.1 Total Residue is defined as the sum of the homogenous suspended and dissolved materials in a sample.
4. Sample Handling and Preservation
   - 4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   - 5.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.
6. Apparatus
   - 6.1 Evaporating dishes, porcelain, 90 mm, 100 ml capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required.)
7. Procedure
   - 7.1 Heat the clean evaporating dish to 103–105°C for one hour, if Volatile Residue is to be measured, heat at 550 ±50°C for one hour in a muffle furnace. Cool, desiccate, weigh and store in desiccator until ready for use.
   - 7.2 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.
     - 7.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.
     - 7.2.2 If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.

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7.3 Dry the evaporated sample for at least 1 hour at 103–105°C. Cool in a desiccator and weigh. Repeat the cycle of drying at 103–105°C, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

8. Calculation

8.1 Calculate total residue as follows:

$$\text{Total residue, mg/l} = \frac{(A - B)\times 1{,}000}{C}$$

where:

A = weight of sample + dish in mg
B = weight of dish in mg
C = volume of sample in ml

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 91, Method 208A, (1975).

EPA METHOD
NO. 120.1

CONDUCTANCE

Method 120.1 (Specific Conductance, umhos at 25°C)

STORET NO. 00095

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
   2.2 Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.
3. Comments
   3.1 Instrument must be standardized with KCl solution before daily use.
   3.2 Conductivity cell must be kept clean.
   3.3 Field measurements with comparable instruments are reliable.
4. Precision and Accuracy
   4.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as Bias, %	Accuracy as Bias, umhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

   4.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 umhos/cm at 25°C, the standard deviation was ±6.

5. References
   5.1 The procedure to be used for this determination is found in:
   Annual Book of ASTM Standards, Part 31, "Water", Standard D1125-64, p 120 (1976).
   Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 71, Method 205, (1975).

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EPA METHOD
NO. 376.2

SULFIDE

Method 376.2 (Colorimetric, Methylene Blue)

STORET NO. Total 00745
Dissolved 00746

1. Scope and Application
   - 1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.
   - 1.3 The method is suitable for the measurement of sulfide in concentrations up to 20 mg/1.
2. Summary of Method
   - 2.1 Sulfide reacts with dimethyl-p-phenylenediamine (p-aminodimethyl aniline) in the presence of ferric chloride to produce methylene blue, a dye which is measured at a wavelength maximum of 625 nm.
3. Comments
   - 3.1 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form. Dissolved oxygen should not be present in any water used to dilute standards.
   - 3.2 The analysis must be started immediately.
   - 3.3 Color and turbidity may interfere with observations of color or with photometric readings.
4. Apparatus
   - 4.1 Matched test tubes, approximately 125 mm long and 15 mm O.D.
   - 4.2 Droppers, delivering 20 drops/ml. To obtain uniform drops, hold dropper in vertical position and allow drops to form slowly.
   - 4.3 Photometer, use either 4.3.1 or 4.3.2.
     - 4.3.1 Spectrophotometer, for use at 625 nm with cells of 1 cm and 10 cm light path.
     - 4.3.2 Filter photometer, with filter providing transmittance near 625 nm.
5. Reagents
   - 5.1 Amino-sulfuric acid stock solution: Dissolve 27 g N,N-dimethyl-p-phenylenediamine oxalate (p-aminodimethylaniline) in a cold mixture of 50 ml conc. H_2SO_4 and 20 ml distilled water in a 100 ml volumetric flask. Cool and dilute to the mark. If dark discard and purchase fresh reagent. Store in dark glass bottle.
   - 5.2 Amino-sulfuric acid reagent: Dissolve 25 ml amino-sulfuric acid stock solution (5.1) with 975 ml of 1 + 1 H_2SO_4 (5.4). Store in a dark glass bottle. This solution should be clear.
   - 5.3 Ferric chloride solution: Dissolve 100 g $FeCl_3 \cdot 6H_2O$ in 40 ml distilled water.

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5.4 Sulfuric acid solution, H_2SO_4, 1 + 1

5.5 Diammonium hydrogen phosphate solution: Dissolve 400 g $(NH_4)_2HPO_4$ in 800 ml distilled water.

5.6 Methylene blue solution I: Dissolve 1.0 g of methylene blue in distilled water in a 1 liter volumetric flask and dilute to the mark. Use U.S.P. grade or one certified by the Biological Stain Commission. The dye content reported on the label should be 84% or more. Standardize (5.8) against sulfide solutions of known strength and adjust concentration so that 0.05 ml (1 drop) equals 1.0 mg/1 sulfide.

5.7 Methylene blue solution II: Dilute 10.00 ml of adjusted methylene blue solution I (5.6) to 100 ml with distilled water in a volumetric flask.

5.8 Standardization of methylene blue I solution:

5.8.1 Place several grams of clean, washed crystals of sodium sulfide $Na_2S\cdot 9H_2O$ in a small beaker.

5.8.2 Add somewhat less than enough water to cover the crystals.

5.8.3 Stir occasionally for a few minutes. Pour the solution into another vessel. This reacts slowly with oxygen but the change is insignificnat over a few hours. Make the solution daily.

5.8.4 To 1 liter of distilled water add 1 drop of solution and mix.

5.8.5 Immediately determine the sulfide concentration by the methylene blue procedure (6) and by the titrimetric iodide procedure (Method 376.1, this manual).

5.8.6 Repeat using more than one drop of sulfide solution or less water until at least five tests have been made in the range of 1 to 8 mg/1 sulfide.

5.8.7 Calculate the average percent error of the methylene blue procedure (6) as compared to the titrimetric iodide procedure (Method 376.1).

5.8.8 Adjust by dilution or by adding more dye to methylene blue solution I (5.6).

6. Procedure

6.1 Color development

6.1.1 Transfer 7.5 ml of sample to each of two matched test tubes using a special wide tipped pipet or filling to a mark on the test tubes.

6.1.2 To tube A add 0.5 ml amine-sulfuric acid reagent (5.2) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3).

6.1.3 Mix immediately by inverting the tube only once.

6.1.4 To tube B add 0.5 ml 1 + 1 H_2SO_4 (5.4) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3) and mix.

6.1.5 Color will develop in tube A in the presence of sulfide. Color development is usually complete in about 1 minute, but a longer time is often required for the fading of the initial pink color.

6.1.6 Wait 3 to 5 minutes.

6.1.7 Add 1.6 ml $(NH_4)_2HPO_4$ solution (5.5) to each tube.

6.1.8 Wait 3 to 5 minutes and make color comparisons. If zinc acetate was used wait at least 10 minutes before making comparison.

6.2 Color comparison

6.2.1 Visual

6.2.1.1 Add methylene blue solution I (5.6) and/or II (5.7) (depending on sulfide concentration and accuracy desired) dropwise to tube B (6.1.4) until the color matches that developed in the first tube.

6.2.1.2 If the concentration exceeds 20 mg/1, repeat 6.2.1.1 using a portion of the sample diluted to one tenth.

6.2.2 Photometric

6.2.2.1 Use a 1 cm cell for 0.1 to 2.0 mg/1. Use a 10 cm cell for up to 20 mg/1.

6.2.2.2 Zero instrument with portion of sample from tube B (6.1.4).

6.2.2.3 Prepare calibration curve from data obtained in methylene blue standardization (5.8), plotting concentraton obtained from titrimetric iodide procedure (Method 376.1) versus absorbance. A straight line relationship can be assumed from 0 to 1.0 mg/1.

6.2.2.4 Read the sulfide concentration from the calibration curve.

7. Calculations

7.1 Visual comparison: With methylene blue solution I (5.6), adjusted so that 0.05 ml (1 drop) = 1.0 mg/1 sulfide and a 7.5 ml sample

mg/1 sulfide = number drops methylene blue solution I (5.6) + 0.1 x [number of drops methylene blue solution II (5.7)].

7.2 Photometric: see 6.2.2.4

8. Precision and Accuracy:

8.1 The precision has not been determined. The accuracy is about ±10%.

Bibliography

1. Standard Methods for he Examination of Water and Wastewater, 14th edition, p. 503, Method 428C (1975).

EPA METHOD
NO. 415.1

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/l.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

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4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

EPA METHOD
NO. 9060

METHOD 9060

TOTAL ORGANIC CARBON

1.0 SCOPE AND APPLICATION

1.1 Method 9060 is used to determine the concentration of organic carbon in ground water, surface and saline waters, and domestic and industrial wastes. Some restrictions are noted in Sections 2.0 and 3.0.

1.2 Method 9060 is most applicable to measurement of organic carbon above 1 mg/L.

2.0 SUMMARY OF METHOD

2.1 Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by either catalytic combustion or wet chemical oxidation. The CO_2 formed is then either measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, the manner of preliminary sample treatment as well as the instrument settings will determine which forms of carbon are actually measured. The forms of carbon that can be measured by Method 9060 are:

1. Soluble, nonvolatile organic carbon: e.g., natural sugars.
2. Soluble, volatile organic carbon: e.g., mercaptans, alkanes, low molecular weight alcohols.
3. Insoluble, partially volatile carbon: e.g., low molecular weight oils.
4. Insoluble, particulate carbonaceous materials: e.g., cellulose fibers.
5. Soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter: e.g., oily matter adsorbed on silt particles.

2.3 Carbonate and bicarbonate are inorganic forms of carbon and must be separated from the total organic carbon value. Depending on the instrument manufacturer's instructions, this separation can be accomplished by either a simple mathematical subtraction, or by removing the carbonate and bicarbonate by converting them to CO_2 with degassing prior to analysis.

3.0 INTERFERENCES

3.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter-type syringe or pipet. The openings of the syringe or pipet limit the maximum size of particle which may be included in the sample.

3.3 Removal of carbonate and bicarbonate by acidification and purging with nitrogen, or other inert gas, can result in the loss of volatile organic substances.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

4.2 Apparatus for total and dissolved organic carbon:

4.2.1 Several companies manufacture analyzers for measuring carbonaceous material in liquid samples. The most appropriate system should be selected based on consideration of the types of samples to be analyzed, the expected concentration range, and the forms of carbon to be measured.

4.2.2 No specific analyzer is recommended as superior. If the technique of chemical oxidation is used, the laboratory must be certain that the instrument is capable of achieving good carbon recoveries in samples containing particulates.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities, and should be boiled and cooled to remove CO_2.

5.2 Potassium hydrogen phthalate, stock solution, 1,000 mg/L carbon: Dissolve 0.2128 g of potassium hydrogen phthalate (primary standard grade) in Type II water and dilute to 100.0 mL.

NOTE: Sodium oxalate and acetic acid are not recommended as stock solutions.

5.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with Type II water.

5.4 Carbonate-bicarbonate, stock solution, 1,000 mg/L carbon: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100-mL volumetric flask. Dissolve with Type II water.

5.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to Step 5.3.
NOTE: This standard is not required by some instruments.

5.6 Blank solution: Use the same Type II water as was used to prepare the standard solutions.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.
NOTE: A brief study performed in the EPA Laboratory indicated that Type II water stored in new, 1-qt cubitainers did not show any increase in organic carbon after 2 weeks' exposure.

6.3 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between sample collection and the start of analysis should be minimized. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

6.4 In instances where analysis cannot be performed within 2 hr from time of sampling, the sample is acidified ($pH \lesssim 2$) with HCl or H_2SO_4.

7.0 PROCEDURE

7.1 Homogenize the sample in a blender.
NOTE: To avoid erroneously high results, inorganic carbon must be accounted for. The preferred method is to measure total carbon and inorganic carbon and to obtain the organic carbon by subtraction. If this is not possible, follow Steps 7.2 and 7.3 prior to analysis; however, volatile organic carbon may be lost.

7.2 Lower the pH of the sample to 2.

7.3 Purge the sample with nitrogen for 10 min.

7.4 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

7.5 For calibration of the instrument, a series of standards should be used that encompasses the expected concentration range of the samples.

7.6 Quadruplicate analysis is required. Report both the average and the range.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Verify calibration with an independently prepared check standard every 15 samples.

8.4 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

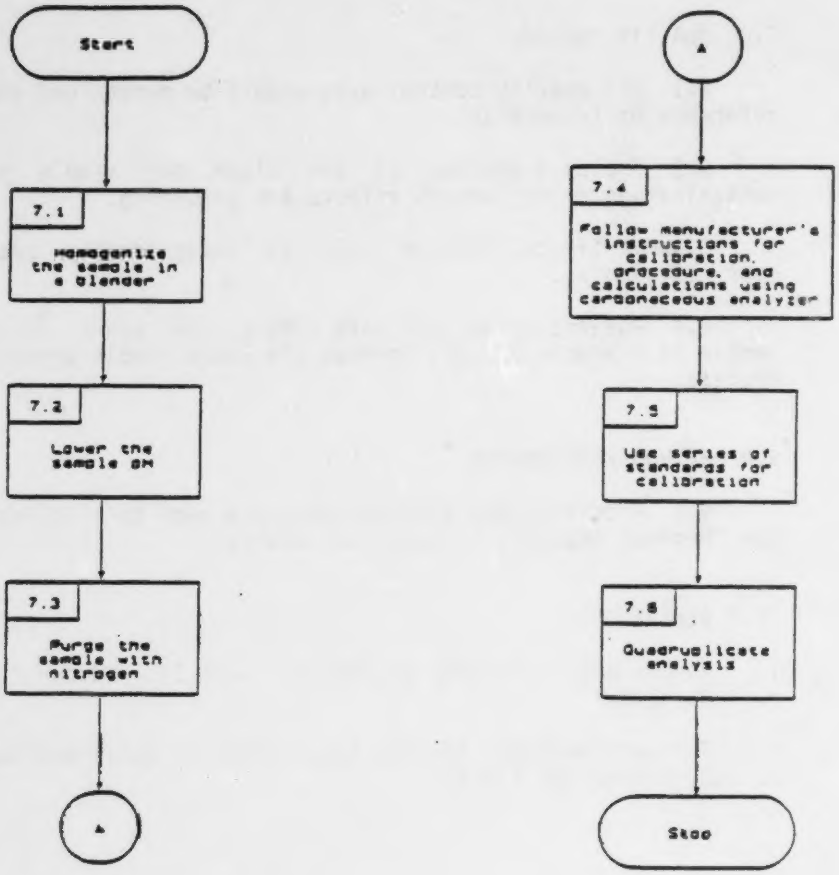
9.1 Precision and accuracy data are available in Method 415.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 532, Method 505 (1975).

METHOD 9060
TOTAL ORGANIC CARBON


Start
7.1
Homogenize the sample in a blender
7.2
Lower the sample pH
7.3
Purge the sample with nitrogen
A
A
7.4
Follow manufacturer's instructions for calibration, procedure, and calculations using carbonaceous analyzer
7.5
Use series of standards for calibration
7.6
Quadruplicate analysis
Stop

EPA METHOD
NO. 415.1M
TOTAL VOLATILE ORGANICS

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured Instrument manufacturer's instructions should be followed.

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Issued 1971
Editorial revision 1974

4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 **Carbonate-bicarbonate, standard solution:** Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 **Blank solution:** Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

Tekmar Company
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LIQUID SAMPLE CONCENTRATOR

MODEL LSC-1

Instruction Manual

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SECTION V REPRINTS AND COMPONENT PARTS INFORMATION

P.O.Box 37202 • Cincinnati, Ohio 45222 • (513) 761-0633 • TELEX NO. 21-4221

Procedure for Purgeable Organic Carbon (POC) of water samples (1944HQ) (Modeled after Method 624).

Water Samples will be analyzed for POC using a Tekmar Model LCS-1 Liquid Sample Concentrator coupled to a Dohrmann Model DC-80 Organic Carbon Analyzer.

The LCS-1 is designed to concentrate volatile organic contaminants found in water samples. By sparging an aliquot of the water sample with an inert purge gas (Zero Grade Nitrogen), the volatile organic contaminants exhibiting low solubility in water will be quantitatively partitioned into the gas phase. The organics from the gas phase will be absorbed on a trap column in the LCS-1 completing the concentration step.

Following the concentration step, the sample is thermally desorbed from the trap column and transferred to the DC-80 by backflushing with Zero Grade Nitrogen. The transfer lines between the trap column and the DC-80 are heated and maintained at 80 degrees to ensure quantitative transfer of the sample.

Operational Parameters of LCS-1

Purge Mode
Purge Gas: Zero Grade Nitrogen (prepurified through a hydrocarbon trap)
Purge Gas Flow: 40 +/- 4 ml/min.
Sample Size: 5.0 ml
Purge Time: 11.0 +/- 0.1 minutes
Purge Temperature: 20 - 25 degrees celcius

Desorbed Mode
Desorb Gas: Zero Grade Nitrogen
Desorb Gas Flow: 20 - 60 ml/min.
Trap Temperature: 170 - 180 degrees celcius
Desorb Time: 4 minutes

Trap
25 cm length
0.12 in ID
Inlet end: 1 cm 3% OV-1 on Chromosorb-W (60/80 Mesh)
Middle: 15 cm of Tenax (60/80 Mesh)
Back End: 8 cm of Silica Gel (35/60 Mesh) grade - 15

SECTION I INTRODUCTION

The LSC-1 is designed to concentrate volatile organic contaminants found in fresh and waste water. By bubbling an inert gas through the aqueous sample, the volatile organic contaminants exhibiting low solubility in water will be quantitatively partitioned into the gas phase. A trap column in the LSC-1 concentrates the organics from the gas phase to complete the concentration step. Following the concentration step (Purge Mode, Figure 2) the sample is thermally desorbed from the trap column (Desorb Mode, Figure 3) and transferred via connecting tubing to your measurement device.

The technique will quantitatively remove those organics exhibiting high volatility (less than 150°C Boiling Point) and low solubility (less than 5%) in water. At solubilities greater than 5% (apx.) partitioning of the organic compound is not quantitative. In the latter case, quantitative analysis is possible by relating the amount of sample partitioned from the aqueous phase to the volume of purge gas used.

SECTION II INSTALLATION

1. Utilities Required:

Power: 110V, 60 Hz, 2A

Gases: Purge gas should be zero grade Helium or Nitrogen. Connect to Purge Gas on rear of LSC-1. Set delivery pressure to 20 psi. A hydrocarbon trap should be used to scrub the purge gas before entering the LSC-1.

Desorb gas should be pre-purified grade Helium or Nitrogen. Connect to Desorb Gas on rear of LSC-1. Delivery pressure will be determined by type of interfacing used. (See Section II, 3 for further details on desorb gas.)

2. Assembly

Except for the sampler, the LSC-1 is completely assembled. Remove the sampler from its packing and install as pictured in Figure 1. The sampler is supported by the 1/4" compression fitting attached to the front panel bracket. Connect the purge gas tube (left side of bracket) to the sampler arm running to the bottom of the frit. Connect the exit tube (right side of bracket) to the right arm of the sampler. Reasonable care should be exercised in attaching the fittings to avoid breakage of the sampler.

3. Interfacing with a Gas Chromatograph

Interfacing to a G.C. is best done by using the G.C. carrier gas as the desorb gas for the LSC-1 (see Figure 4). The output of the G.C. flow controller is connected directly to the desorb gas input of the LSC-1. The trap effluent port on the LSC-1 is connected directly to the carrier input of the G.C. injection port using the 1/8" O.D. teflon tubing supplied. Using this type of interfacing, the G.C. carrier backflushes the LSC-1 trap directly to the G.C. column in Desorb Mode. In Purge Mode, operation of the G.C. is unaffected.

An alternate means of interfacing to a G.C. is the tube-needle coupling (see Figure 5). In this case the trap effluent port of the LSC-1 is connected to the septa injector of the G.C. with teflon tubing and needle adaptor (supplied with LSC-1.) Desorb gas for the LSC-1 must be supplied at a pressure greater than the pressure of the carrier gas going to the G.C. (to prevent G.C. carrier from backstreaming to the LSC-1 during Desorb Mode.) A flow rate of 20 cc/min. for the desorb gas is sufficient. An auxiliary flow controller is required between the desorb gas tank and the LSC-1 to regulate the desorb flow.

4. Interfacing with a Totals Detector

Interfacing to a totals detector (specific chlorine, TOC analyzer, total hydrocarbon analyzer, etc.) is usually accomplished using the tube-needle coupling (Figure 6). However, if the totals detector uses a carrier gas, that carrier could be used as the desorb gas for the LSC-1 (Figure 4).

5. Conditioning Trap Column

The trap column in your LSC-1 was baked out prior to shipment but should be baked again prior to operation. Turn on the LSC-1, set the Purge/Desorb valve to Purge, set the Trap Bake/Operate switch to Trap Bake, and set the Trap Temperature Control to 250°C.

Leave the LSC-1 in this condition overnight for a thorough cleaning of the trap. This procedure can be repeated whenever trap contamination is suspected.

SECTION III OPERATION

1. Description of Controls

Trap Bake/Operate

Operate:	Trap oven and fan are controlled by position of purge/desorb valve. Purge timer can be set for desired purge time.
Trap Bake:	Used for conditioning trapping column. Fan is off and the oven is on independent of purge/desorb valve position. (The purge/desorb valve should be set in the purge position during trap bake mode to avoid contamination of the measurement device.
Trap Temperature Control:	This is a direct set proportional temperature controller. The red light below the control blinks when the controller is proportioning at the set temperature. The control is off in purge mode. For all other instrument settings, the controller is on. The range is room temperature to 350°C.
Purge Timer:	The timer controls a three-way valve supplying purge gas to the sampler. The timer can be set from zero to thirty minutes and is continuously adjustable. After setting the time, the timer is started by pressing the white button in the center of the

timer knob. At the end of the pre-set time the purge valve closes and the timer re-sets itself. To terminate a run, rotate the timer knob counter-clockwise to zero.

Purge/Desorb:

Purge:	The flow of purge gas (controlled by rotameter and purge timer) is directed to the trap column and to vent. The desorb gas passes through the valve, by-passing the trap column enroute to the measurement device (Figure 2).
Desorb:	The sampler is connected to vent and the desorb gas backflushes the heated trap column enroute to the measurement device (Figure 3).
Purge Flow:	Flowmeter used to establish the flow of purge gas to the sampler.
Trap Effluent:	For connection to measurement unit.
Injection Port:	Located on top of front panel bracket and uses standard G.C. septa.

2. Operation

Set main power switch to On (no warm-up required) and set Trap Bake/Operate switch to Operate. Establish a 40 cc/min. flow rate of purge gas with the flowmeter (approximately 45 on the flowmeter, but this must be checked against a bubble type flowmeter or similar calibrating device.) Set the Trap Temperature Control to 180°C. Fill the 5 ml syringe with sample by removing the plunger and pouring sample into the barrel to overflowing. Open the valve on the bottom of the syringe and reinsert the plunger into the syringe barrel (avoid air bubbles between the liquid and plunger.) Using the long needle, the sample is injected into the purge unit. (If the sample is not injected immediately, close the syringe valve to avoid loss of volatiles.)

Set the purge timer to the required purge time (typically 11 minutes), and press the white button in the center of the timer knob. Purge gas will now be bubbling through the sample and will stop automatically at the end of the pre-set purge time. During this interval, prepare your measurement device to receive the sample. The concentrated sample is transferred to your measurement unit by turning the Desorb/Purge valve to Desorb. This backflushes the trap column and turns on the Temperature Controller, causing a rapid temperature rise in the trap and thermal desorption. After three or four minutes, return the system to purge mode and the LSC-1 is ready to accept a new sample.

As mentioned above, the LSC-1 needs no warm-up. Indeed, if long delays occur between sample runs, it would be best to turn off the LSC-1 to avoid needless running of the trap column cooling fan.

3. Calibration

Prepare a solution of your standards in methanol at a concentration of 1000 times the desired calibration level. Inject 5 ul of the methanol solution directly into the 5 ml sample syringe containing organic free water using the 10 ul syringe supplied with the LSC-1. The 10 ul syringe needle is run through the valve attached to the 5 ml sample syringe with the valve in the open position. After injecting the standard into the organic free water, withdraw the 10 ul syringe, close the valve, attach the long needle to the valve and inject the 5 ml into the purge unit.

4. Trap Column

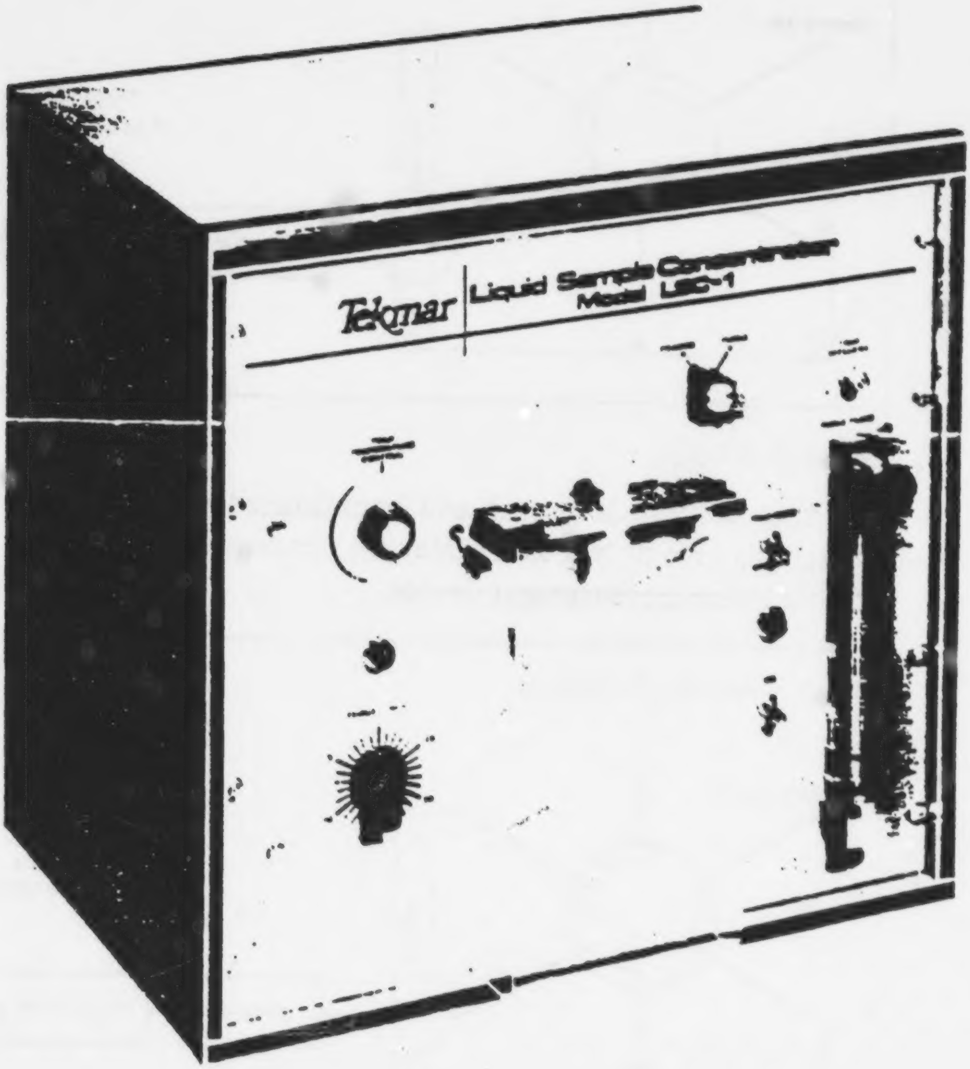
The trap installed in your LSC-1 contains 2/3 Tenax and 1/3 Silica Gel Davisson Grade 15. This is optimized for trapping organohalides but will also trap a broad range of organic compounds. A blank trap is supplied for making your own trap column if it is desired to optimize for a particular compound. The top of the column is identified by two grooves cut near the top end. An all tenax trap is available and is identified by one groove cut near the top end.

The trap column is accessible through the rear panel.

CAUTION: Unplug power cord before removing the back panel or chassis.

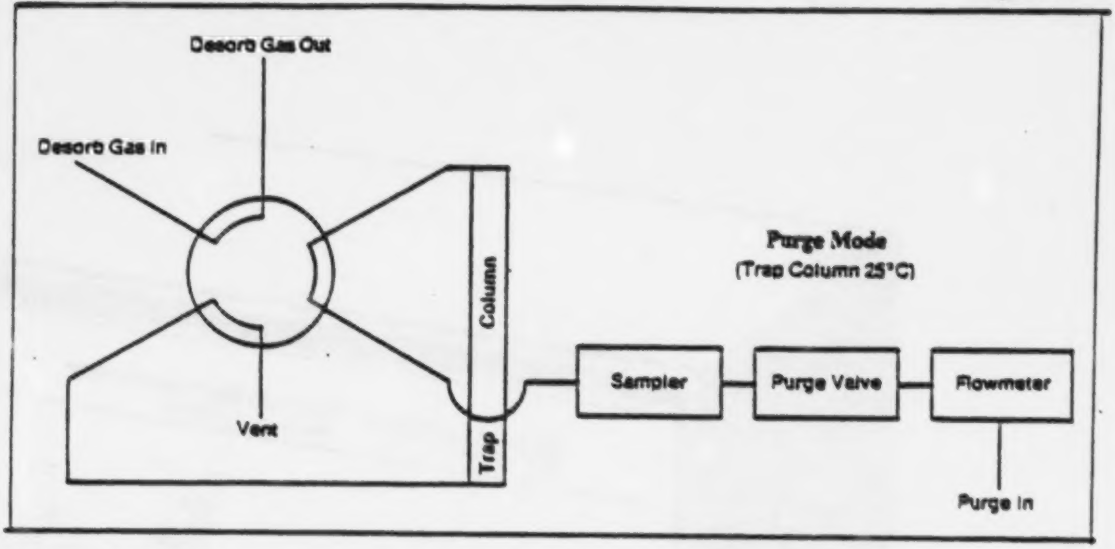
The fittings at the top of the trap are finger tight and utilize teflon ferrules. Remove the 1/16" tube and fitting from the top of the trap and loosen the fitting at the base. Lift the trap vertically about one inch. Swing the bottom of the trap to the rear of the LSC-1 and the trap and furnace can be removed through the opening in the rear of the furnace housing.

Figure 1


Tekmar
Liquid Sample Concentrator
Model LSC-1

Purge gas (He or N_2) is bubbled through the sample, partitioning volatile organics into the gas phase for concentration by the trap column.

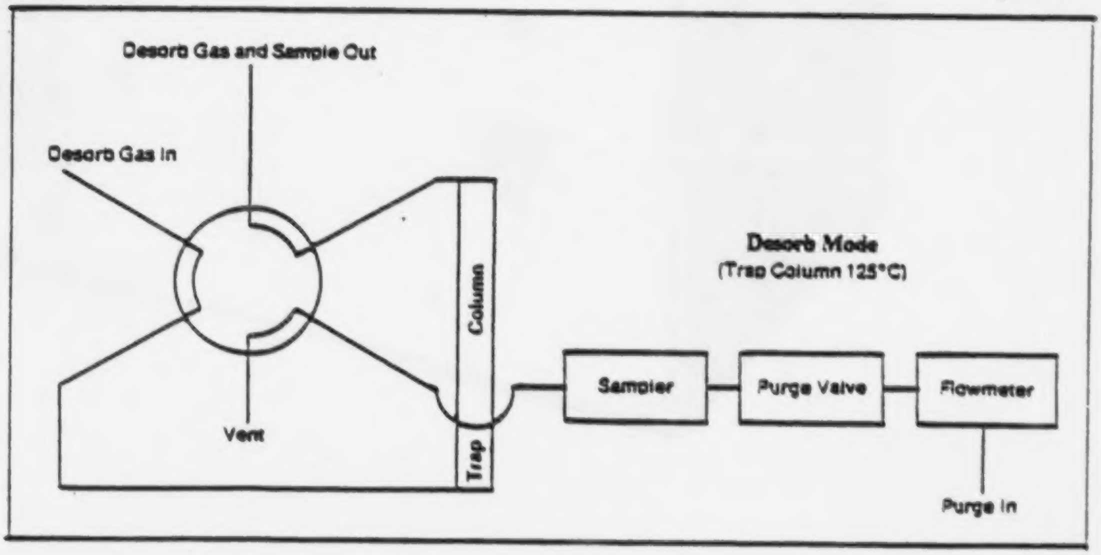
Figure 2


Desorb Gas Out
Desorb Gas In
Column
Purge Mode
(Trap Column 25°C)
Sampler
Purge Valve
Flowmeter
Vent
Trap
Purge In

Desorb Mode

The trap column is heated and backflushed with carrier gas (He or N_2) to transfer the concentrated sample to the measurement device.

Figure 3


Desorb Gas and Sample Out
Desorb Gas In
Column
Desorb Mode
(Trap Column 125°C)
Sampler
Purge Valve
Flowmeter
Vent
Trap
Purge In

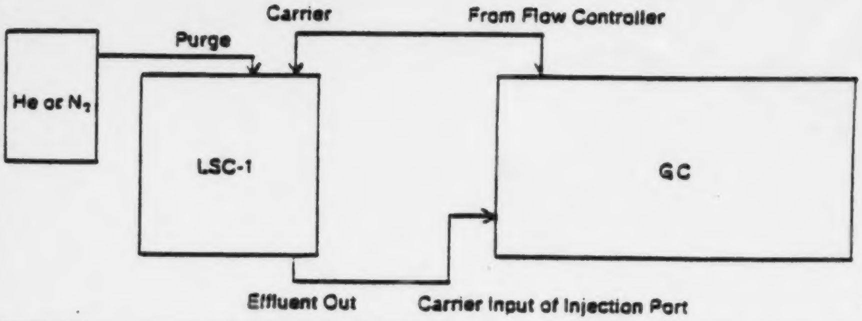
Bake Mode

This is a service mode for cleaning the trap column at elevated temperature while venting the effluent to atmosphere.

LSC-1 Typical Detector Interfacings

LSC-1/GC

Direct couple to GC using GC carrier as LSC-1 input.

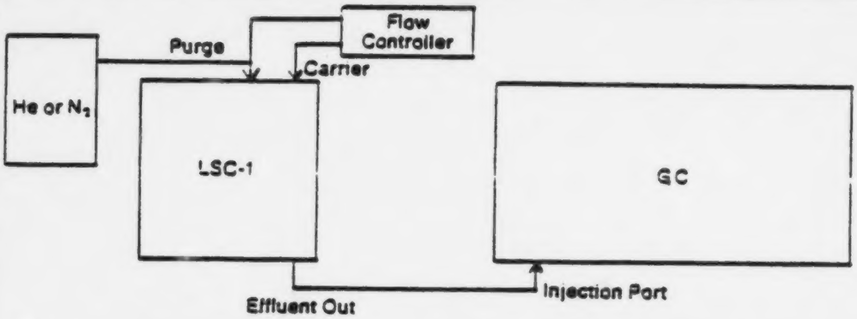


Carrier
From Flow Controller
Purge
He or N_2
LSC-1
GC
Effluent Out
Carrier Input of Injection Port

Figure 4

LSC-1/GC

Tube-needle coupling to GC using alternate source of He or N_2 as LSC-1 carrier input.

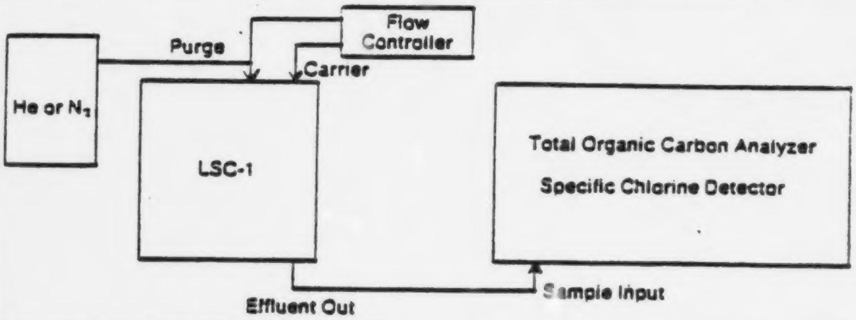


Flow Controller
Purge
Carrier
He or N_2
LSC-1
GC
Effluent Out
Injection Port

Figure 5

LSC-1/Specific Totals Detector

Tube-needle coupling to totals detector using alternate source of He or N_2 as LSC-1 carrier input.



Flow Controller
Purge
Carrier
He or N_2
LSC-1
Total Organic Carbon Analyzer
Specific Chlorine Detector
Effluent Out
Sample Input

Figure 6

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EPA METHOD
NO. 1010

METHOD 1010[1]

PENSKY-MARTENS CLOSED-CUP METHOD

1.0 Scope and Application

1.1 Method 1010 uses the Pensky-Martens closed-cup tester to determine the flash point of fuel oils, lube oils, suspensions of solids, liquids that tend to form a surface film under test conditions, and other liquids.

2.0 Summary of Method

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

3.0 Interferences

3.1 Ambient pressure, sample homogeneity, drafts, and operator bias can affect flash point values.

4.0 Apparatus

4.1 Pensky-Martens Closed Flash Tester, as described in Annex A1 of ASTM Method D93-77. (Automatic flash point testers are available and may be advantageous since they save testing time, permit the use of smaller samples, and exhibit other advantages. If automatic testers are used, the user must be sure to follow all the manufacturer's instructions for calibrating, adjusting, and operating the instrument. In any cases of dispute, the flash point as determined manually shall be considered the referee test.)

4.2 Thermometers: Two standard thermometers shall be used with the ASTM Pensky-Martens tester.

4.2.1 For tests in which the indicated reading falls within -7° to +110° C (20° to 230° F), inclusive: either (1) an ASTM Pensky-Martens Low Range or Tag Closed Tester Thermometer having a range from -7° to +110° C (20° to 230° F) and conforming to the requirements for Thermometers 9C (9F) and as prescribed in ASTM Specification E1, or (2) an IP Thermometer 15C (15F) conforming to specifications given in Annex A3 of ASTM D93-77.

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[1] This method is based on ASTM Method D93-77. Refer to D93-77 or D93-80 for more information.

4.2.2 For tests in which the indicated reading falls within 110° to 370° C (230° to 700° F): either (1) an ASTM Pensky-Martens High Range Thermometer having a range from 90° to 370° C (200° to 700° F) and conforming to the requirements for Thermometers 10C (10F) as prescribed in Specification E1, or (2) IP Thermometer 16C (16F) conforming to specifications given in Annex A3 of ASTM D93-77.

5.0 Reagents

5.1 Calcium chloride.

5.2 p-Xylene reference standard.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples shall not be stored in plastic bottles since volatile materials may diffuse through the walls of the bottle.

7.0 Procedure

7.1 Preparation of samples: Samples that do not contain volatile contaminants shall be prepared in the following manner. NOTE: If the sample is suspected of containing volatile contaminants, the treatment described in 7.1.1 and 7.1.2 should be omitted.

7.1.1 Samples of very viscous materials may be warmed until they are reasonably fluid before they are tested. However, no sample should be heated more than is absolutely necessary, and no sample should ever be heated to a temperature that exceeds 17° C (30° F) below the sample's expected flash point.

7.1.2 Samples containing dissolved or free water may be dehydrated with calcium chloride or by filtering through a qualitative filter paper or a loose plug or dry absorbent cotton. Warming the sample is permitted, but it shall not be heated for prolonged periods or above a temperature of 17° C (30° F) below the sample's expected flash point.

7.2 Routine procedure

7.2.1 Thoroughly clean and dry all parts of the cup and its accessories before starting the test. Be sure to remove any solvent that was used to clean the apparatus. Fill the cup with the sample to be tested to the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove. Be sure to properly engage the locating or locking device. Insert the thermometer. Light the test flame and adjust it to a diameter of 5/32 in. (4 mm). Supply the heat at such a rate that the temperature as indicated by the thermometer increases 5° to 6° C (9° to 11° F)/min. Turn the stirrer 90 to 120 rpm, stirring in a downward direction.

7.2.2 If the sample is expected to have a flash point of 110° C (230° F) or below, apply the test flame when the temperature of the sample is from 17° C (30° F) to 28° C (50° F) below the expected flash point and thereafter at a temperature reading that is a multiple of 1° C (2° F). Apply the test flame by operating the mechanism on the cover which controls the shutter and test flame burner so that the flame is lowered into the vapor space of the cup in 0.5 sec, left in its lowered position for 1 sec, and quickly raised to its high position. Do not stir the sample while applying the test flame.

7.2.3 If the sample is expected to have a flash point above 110° C (230° F), apply the test flame in the manner just described at each temperature that is a multiple of 2° C (5° F), beginning at a temperature of 17° C (30° F) to 28° C (50° F) below the expected flash point. NOTE: When testing materials to determine if volatile contaminants are present, it is not necessary to adhere to the temperature limits for initial flame application as stated in 7.2.2 and 7.2.3.

7.2.4 Record as the flash point the temperature read on the thermometer at the time the test flame application causes a distinct flash in the interior of the cup. Do not confuse the true flash point with the bluish halo that sometimes surrounds the test flame at applications preceding the one that causes the actual flash. The actual flash will have occurred when a large flame propagates itself over the surface of the sample.

7.3 Determination of flash point of suspensions of solids and highly viscous materials

7.3.1 Bring the material to be tested and the tester to a temperature of 15° ± 5° C (60° ± 10° F) or 11° C (20° F) lower than the estimated flash point, whichever is lower. Turn the stirrer 250 ± 10 rpm, stirring in a downward direction. Raise the temperature throughout the duration of the test at a rate of not less than 1° nor more than 1.5° F (2 to 3° F)/min. With the exception of these requirements for rates of stirring and heating, proceed as prescribed in Section 7.2.

7.4 Calculation and report

7.4.1 Observe and record the ambient barometric pressure at the time of the test. When the pressure differs from 760 mm Hg (101.3 kPa), correct the flash point as follows:

(A) Corrected flash point = $C + 0.25\ (101.3 - p)$

(B) Corrected flash point = $F + 0.06\ (760 - P)$

(C) Corrected flash point = $C + 0.033\ (760 - P)$

where:

F = observed flash point, °F

C = observed flash point, °C

P = ambient barometric pressure, mm Hg

p = ambient barometric pressure, kPa.

NOTE: The barometric pressure used in this calculation must be the ambient pressure for the laboratory at the time of test. Many aneroid barometers, such as those used at weather stations and airports, are precorrected to give sea level readings. These must not be used.

7.4.2 Record the corrected flash point to the nearest 0.5° C (or 1° F).

7.4.3 Report the recorded flash point as the Pensky-Martens Closed Cup Flash Point ASTM D93 - IP 34, of the sample tested.

7.5 Refer to Method ASTM D93 77 for more details and background on the Pensky-Marten method.

8.0 Quality Control

8.1 All quality control data should be available for review.

8.2 Duplicates and standard reference materials should be routinely analyzed.

8.3 The flash point of the p-xylene reference standard must be determined in duplicate at least once per sample batch. The average of the two analyses should be 27° ± 0.8° C (81° ± 1.5° F).

EPA METHOD
NO. 1110

METHOD 1110

CORROSIVITY TOWARD STEEL

1.0 Introduction

1.1 Method 1110[1] is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

2.0 Summary of Method

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

3.0 Interferences

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within ± 10%. However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

4.0 Apparatus and Materials

4.1 A versatile and convenient apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5000 milliliters), a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type test is shown in Figure 1.

4.2 The supporting device and container should not be affected by or cause contamination of the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test but should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon or coated metal.

---

[1] This method is based on NACE Standard TM-01-69 (1972 Revision), "Laboratory Corrosion Testing of Metals for the Process Industries," National Association of Corrosion Engineers, 3400 West Loop South, Houston, TX 77027.

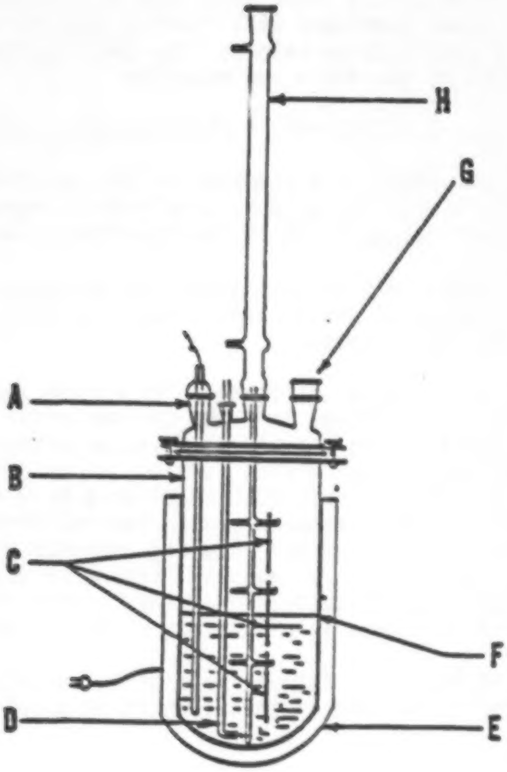

Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = gas inlet, E = heating mantle, F = liquid interface, G = opening in flask for additional apparatus that may be required, and H = reflux condenser.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 inch) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 inch) and a 0.80-cm (0.4-in.) diameter hold for mounting, these specimens will readily pass through a 45/50 ground glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2-d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where t = thickness, D = diameter of the specimen, and d = diameter of the mounting hole. If the hole is completely covered by the mounting support, the last term (t)(3.14)(d) in the equation is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to ± 1% is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished either by chemical treatment (pickling), electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 inch) or 2 to 3 mg/cm^2 should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleachfree scouring powder, followed by rinsing in distilled water, then acetone or methanol, and finally air drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 ml/cm^2.

5.0 Reagents

5.1 Sodium hydroxide (20%).

5.2 Zinc dust.

5.3 Concentrated hydrochloric acid.

5.4 Stannous chloride.

5.5 Antimony chloride.

6.0 Sample Collection, Presentation, and Handling

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

7.0 Procedure

7.1 Assemble the test apparatus as described in Section 4.0 above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device bring the temperature of the waste to 55° C (130° F).

7.5 An accurate rate of corrosion is not required but only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year. A 24-hour test period should be ample to determine whether or not the rate of corrosion is greater than 6.35 mm per year.

7.6 In order to accurately determine the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease or resinous materials, and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

Solution	Soaking Time	Temperature
20% NaOH + 200 g/l zinc dust	5 min	Boiling
or		
Conc. HCl + 50 g/l $SnCl_2$ + 20 g/l $SbCl_3$	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed is:

Solution	50 g/l H_2SO_4
Anode	Carbon or lead
Cathode	Steel coupon
Cathode current density	20 amp/cm^2 (129 amp/in.^{2})
Inhibitor	2 cc organic inhibitor/liter
Temperature	74° C (165° F)
Exposure Period	3 minutes

NOTE: Precautions must be taken to ensure good electrical contact with the coupon, to avoid contamination of the cleaning solution with easily reducible metal ions, and to ensure that inhibitor decomposition has not occurred. Instead of using a proprietary inhibitor, 0.5 g/l or either diorthotolyl thiourea or quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighed. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss} \times 11.145}{\text{area} \times \text{time}}$$

where weight loss is in milligrams, area in square centimeters, time in hours, and corrosion rate in millimeters per year (mmpy).

8.0 Quality Control

8.1 All quality control data should be filed and available for auditing.

8.2 Duplicate samples should be analyzed on a routine basis.

HAZARDOUS WASTE CHARACTERISTICS
-REACTIVITY-
(FROM SW 846)

2.1.3 Reactivity

Introduction

The regulation in 40 CFR 261.23 defines reactive wastes to include wastes which have any of the following properties: (1) readily undergo violent chemical change; (2) react violently or form potentially explosive mixtures with water; (3) generate toxic fumes when mixed with water or, in the case of cyanide or sulfide-bearing wastes, when exposed to mild acidic or basic conditions; (4) explode when subjected to a strong initiating force; (5) explode at normal temperatures and pressures; or (6) fit within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classifications.

This definition is intended to identify wastes which, because of their extreme instability and tendency to react violently or explode, pose a problem at all stages of the waste management process. The definition is to a large extent a paraphrase of the narrative definition employed by the National Fire Protection Association. The Agency chose to rely on a descriptive, prose definition of reactivity because the available tests for measuring the variegated class of effects embraced by the reactivity definition suffer from a number of deficiencies.

Regulatory Definition

Characteristic of Reactivity Regulation

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

1. It is normally unstable and readily undergoes violent change without detonating.

2. It reacts violently with water.

3. It forms potentially explosive mixtures with water.

4. When mixed with water, it generates toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment.

5. It is a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment. (Methods 9010 and 9030 can be used to detect the presence of cyanide and sulfide in wastes.)

6. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

7. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

8. It is a forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

9. A solid waste that exhibits the characteristic of reactivity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number of D003.

Definition of Explosive Materials

For purposes of this regulation, a waste is a reactive waste by reason of explosivity if it meets one or more of the following descriptions:

1. Is explosive and ignites spontaneously or undergoes marked decomposition when subjected for 48 consecutive hours to a temperature of 75° C (167° F).

2. Firecrackers, flash crackers, salutes, or similar commercial devices which produce or are intended to produce an audible effect, the explosive content of which exceeds 12 grains each in weight; pest control bombs, the explosive content of which exceeds 18 grains each in weight; and any such devices, without respect to explosive content, which on functioning are liable to project or disperse metal, glass or brittle plastic fragments.

3. Fireworks that combine an explosive and a detonator or blasting cap.

4. Fireworks containing an ammonium salt and a chlorate.

5. Fireworks containing yellow or white phosphorus.

6. Fireworks or firework compositions that ignite spontaneously or undergo marked decomposition when subjected for 48 consecutive hours to a temperature of 75° C (167° F).

7. Toy torpedoes, the maximum outside dimension of which exceeds 7/8 inch, or toy torpedoes containing a mixture of potassium chlorate, black antimony and sulfur with an average weight of explosive composition in each torpedo exceeding four grains.

8. Toy torpedoes containing a cap composed of a mixture of red phosphorus and potassium chlorate exceeding an average of one-half (0.5) grain per cap.

9. Fireworks containing copper sulfate and a chlorate.

10. Explosives containing an ammonium salt and a chlorate.

11. Liquid nitroglycerin, diethylene glycol dinitrate or other liquid explosives not authorized.

12. Explosives condemned by the Bureau of Explosives (except properly packed samples for laboratory examinations).

13. Leaking or damaged packages of explosives.

14. Solid materials which can be caused to deflagrate by contact with sparks or flame such as produced by safety fuse or an electric squib, but cannot be detonated (see Note 1) by means of a No. 8 test blasting cap (see Note 2). Example: Black powder and low explosives.

15. Solid materials which contain a liquid ingredient, and which, when unconfined (see Note 3), can be detonated by means of a No. 8 test blasting cap (see Note 2); or which can be exploded in at least 50 percent of the trials in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of 4 inches or more, but cannot be exploded in more than 50 percent of the trials under a drop of less than 4 inches. Example: High explosives, commercial dynamite containing a liquid explosive ingredient.

16. Solid materials which contain no liquid ingredient and which can be detonated, when unconfined (see Note 3), by means of No. 8 test blasting cap (see Note 2); or which can be exploded in at least 50 percent of the trials in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of 4 inches or more, but cannot be exploded in more than 50 percent of the trials under a drop of less than 4 inches. Example: high explosives, commercial dynamite containing no liquid explosive ingredient, trinitrotoluene, amatol, tetryl, picric acid, ureanitrate, pentolite, commercial boosters.

17. Solid materials which can be caused to detonate when unconfined (see Note 3), by contact with sparks or flame such as produced by safety fuse or an electric squib; or which can be exploded in the Bureau of Explosives' Impact Apparatus (see Note 4), in more than 50 percent of the trials under a drop of less than 4 inches. Example: initiating and priming explosives, lead azide, fulminate of mercury, high explosives.

18. Liquids which may be detonated separately or when absorbed in sterile absorbent cotton, by a No. 8 test blasting cap (see Note 2); but which cannot be exploded in the Bureau of Explosives' Impact Apparatus (see Note 4), by a drop of less than 10 inches. The liquid must not be significantly more volatile than nitroglycerine and must not freeze at temperatures above minus 10° F. Example: high explosives, desensitized nitroglycerine.

19. Liquids that can be exploded in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of less than 10 inches. Example: nitroglycerine.

20. Blasting caps. these are small tubes, usually made of an alloy of either copper or aluminum, or of molded plastic closed at one end and loaded with a charge of initiating or priming explosives. Blasting caps (see Note 5) which have been provided with a means for firing by an electric current, and sealed, are known as electric blasting caps.

21. Detonating primers which contain a detonator and an additional charge of explosives, all assembled in a suitable envelope.

22. Detonating fuses, which are used in the military service to detonate the high explosive bursting charges of projectiles, mines, bombs, torpedoes, and grenades. In addition to a powerful detonator, they may contain several ounces of a high explosive, such as tetryl or dry nitrocellulose, all assembled in a heavy steel envelope. They may also contain a small amount of radioactive component. Those that will not cause functioning of other fuses, explosives, or explosive devices in the same or adjacent containers are classes as class C explosives and are not reactive waste.

23. A shaped charge, consisting of a plastic, paper, or other suitable container comprising a charge of not to exceed 8 ounces of a high explosive containing no liquid explosive ingredient and with a hollowed-out portion (cavity) lined with a rigid material.

24. Ammunition or explosive projectiles, either fixed, semi-fixed or separate components which are made for use in cannon, mortar, howitzer, recoilless rifle, rocket, or other launching device with a caliber of 20 mm or larger.

25. Grenades. Grenades, hand or rifle, are small metal or other containers designed to be thrown by hand or projected from a rifle. They are filled with an explosive or a liquid, gas, or solid material such as a tear gas or an incendiary or smoke producing material and a bursting charge.

26. Explosive bombs. Explosive bombs are metal or other containers filled with explosives. They are used in warfare and include airplane bombs and depth bombs.

27. Explosive mines. Explosive mines are metal or composition containers filled with a high explosive.

28. Explosive torpedoes. Explosive torpedoes, such as those used in warfare, are metal devices containing a means of propulsion and a quantity of high explosives.

29. Rocket ammunition. Rocket ammunition (including guided missiles) is ammunition designed for launching from a tube, launcher, rails, trough, or other launching device, in which the propellant material is a solid propellant explosive. It consists of an igniter, rocket motor, and projectile (warhead) either fused or unfused, containing high explosives or chemicals.

30. Chemical ammunition. Chemical ammunition used in warfare is all kinds of explosive chemical projectiles, shells, bombs, grenades, etc., loaded with tear, or other gas, smoke or incendiary agent, also such miscellaneous apparatus as cloud-gas cylinders, smoke generators, etc., that may be utilized to project chemicals.

31. Boosters, bursters, and supplementary charges. Boosters and supplementary charges consist of a casing containing a high explosive and are used to increase the intensity of explosion of the detonator of a detonating fuse. Bursters consist of a casing containing a high explosive and are used to rupture a projectile or bomb to permit release of its contents.

32. Jet thrust units or other rocket motors containing a mixture of chemicals capable of burning rapidly and producing considerable pressure.

33. Propellant mixtures (i.e., any chemical mixtures which are designed to function by rapid combustion with little or no smoke).

NOTE 1: The detonation test is performed by placing the sample in an open-end fiber tube which is set on the end of a lead block approximately 1-1/2 in. in diameter and 4 in. high which, in turn, is placed on a solid base. A steel plate may be placed between the fiber tube and the lead block.

NOTE 2: A No. 8 test blasting cap is one containing two grams of a mixture of 80% mercury fulminate and 20% potassium chlorate, or a cap of equivalent strength.

NOTE 3: "Unconfined" as used in this section does not exclude the use of a paper or soft fiber tube wrapping to facilitate tests.

NOTE 4: The Bureau of Explosives' Impact Apparatus is a testing device designed so that a guided 8-lb weight may be dropped from predetermined heights so as to impact specific quantities of liquid or solid materials under fixed conditions. Detailed prints of the apparatus may be obtained from the Bureau of Explosives, Association of American Railroads, Operations and Maintenance Dept., Bureau of Explosives, American Railroad Building, Washington, D.C. 20036; 202-293-4048. The procedures for operating this apparatus are described in the following paragraphs.

Method for Testing Liquids. The anvil is inserted in the receptable in the anvil housing. A new cup is dropped into the cup-positioning block. One drop of the sample liquid (about 0.01 g) is dropped into the cup from a pipette and the cup is revolved until an even film forms on base. The top striker and the main striker are inserted as far as possible into the upper housing. The upper housing is then placed over the cup-positioning block so that the end of the main striker goes into the brass cup. When the upper housing is removed from the cup-positioning block, the brass cup is picked up on the end of the main striker. When the two housings are screwed together, the brass cup automatically rests firmly on the anvil.

An 8-lb drop weight is dropped from predetermined heights until consistent failure results using the new sample portion and cup each time. An explosion is evidenced by flame or flame and noise, but in either event the brass cup will be belled out or bulged.

After making the drop, the drop weight is raised, the test assembly removed, and appropriate solvent is poured into the top end. The two housings are then separated, the striker removed, and the brass cup removed from the striker end.

All solvent is removed carefully and thoroughly before preparations are started for next drop and the apparatus cooled and cleaned. The test is then repeated in the same manner, but with a filter paper disc in the base of the cup under the composition being tested.

Method for Testing Solids. The die is placed in the anvil assembly and a small amount (about 0.01 g)[1] to make a thin film is placed into the die assembly. The steel striker pellet (plug) is inserted carefully and then the striker (plunger). The assembly is then placed in the apparatus and the drop weight allowed to rest on the striker top to effect even distribution of the explosive.

The 8-lb drop weight is then dropped on the striker from predetermined heights until consistent failure results (i.e., explosion, etc.) using a new sample portion each time.

The die assembly is removed carefully and the striker removed. A few drops of appropriate solvent are poured into the die assembly before it is disassembled.

All parts are cleaned and dried carefully before each test.

NOTE 5: Blasting caps, blasting caps with safety fuse, or electric blasting caps in quantities of 1,000 or less are classified as class 0 explosives and not subject to regulation as a reactive waste.

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[1] It is suggested that a tiny spoon be devised to measure the proper amount of test sample, since this is much more convenient and safer than other methods of measuring the sample.